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THE REFLECTION OF X-RAYS BY CRYSTALS AS A PROBLEM IN THE REFLECTION OF RADIATION BY PARALLEL PLANES

By Samuel K. Allison

Abstract

It is pointed out that the previous solutions of the problem of the reflection of radiation from parallel planes by Lamson and Gronwall are physically incorrect since the intensities, not the amplitudes, of contributions from individual planes, have been added. It is shown that a mathematical method due to Darwin leads to a solution identical mathematically with those of Lamson and Gronwall. Using this result, the intensity of reflection is evaluated for certain ranges of the constants directly related to the reflected and transmitted amplitudes due to a single plane.

THE problem of the reflection and transmission of radiation by a set of parallel, equidistant, reflecting planes has been treated by Darwin[1], Lamson[2], and recently, Gronwall[3]. The solution of this problem is at least of theoretical interest in the treatment of the intensity of reflection of x-rays by crystals, for if we adopt the Bragg picture of the reflection of x-rays by atomic planes, as contrasted with the space-lattice treatment of Laue, the reflection and transmission of a crystal sheet for an incident x-ray beam is essentially a problem of this type. The treatment of the problem of the reflection of x-rays by the methods used in the optics of isotropic media has been criticised by Ewald[4], but recently Bragg, Darwin and James[5], have pointed out that the methods used by Darwin give results almost identical with those of Ewald.

The treatments of the problem by Lamson and Gronwall, while excellent mathematically, are open to he fundamental objection that in computing the total reflection as a function of the amount reflected from each plane, the *intensities* from each plane have been added. Now in any practical case, and certainly in the crystalline reflection of x-rays, the

[1] Darwin, Phil. Mag. **27**, 675 (1914).
[2] Lamson, Phys. Rev. **17**, 624 (1921).
[3] Gronwall, Phys. Rev. **27**, 277 (1926).
[4] Ewald, Zeits. f. Physik **30**, 1 (1924); Ann d. Physik **54**, 519 (1918).
[5] Bragg, Darwin, and James, Phil. Mag. **1**, 897 (1926).

waves in question are coherent, and instead of their intensities, their *amplitudes* should be added. Nevertheless it can be shown that a large part of the mathematical work laid down by these authors is useful in the physically correct solution of the problem. The mathematical treatment of Gronwall is complete and elegant; he has obtained a solution intended to give the amount of radiation reflected from an incident beam of unit intensity by an infinite number of parallel planes, and also to give the amounts reflected and transmitted by a finite number of planes. The solutions for a finite number of planes are exceedingly complicated when expressed in terms of the constants of one plane and will not be considered here. The principal purpose of this paper is to attempt to give an acceptable physical meaning to the mathematical results of Gronwall for the reflection from an infinite number of parallel planes.

Let us consider the incidence of a monochromatic, parallel (an obvious idealisation), beam of x-rays of unit amplitude upon the face of a perfect crystal at the proper angle for reflection according to the Bragg law. We will neglect the influence of the index of refraction, also the polarisation and temperature corrections etc. According to the Bragg picture we can consider the atoms reflecting the x-rays to be arranged in planes. Let R_1 be the amplitude reflected by a single plane, and let T_1 be the amplitude of the wave emerging from the lower side of the plane, that is, the transmitted amplitude. Let R_n be the amplitude of the total wave reflected by n planes (as it emerges above the crystal face) considering all possible internal multiple reflections, and T_n be the amplitude of the total wave transmitted by n planes. Then following the method of Gronwall it is easily shown that the following equations hold[6].

$$R_{n+1}=R_n+T_n^2R_1/(1-R_1R_n) \tag{1}$$

$$T_{n+1}=T_nT_1/(1-R_1R_n) \tag{2}$$

These are second order difference equations, and if R is the amplitude of reflection from an infinite number of planes, Gronwall has shown[7] that they lead to the result.

[6] These equations may be obtained from Eqs. (8) and (7) of Gronwall's paper by making the substitutions $t=T_1$, $r=R_1$, $R_n'=R_n-R_1$. The introduction of R' terms in Gronwall's treatment is unnecessary.

[7] The radical in (3) comes in as the result of solving a quadratic equation, and Gronwall gives reasons for selecting the proper sign before the radical which are not valid for the case where amplitudes, and not intensities, are added. Nevertheless, an argument valid for the present treatment may be advanced which leads to the same selection of sign. Referring to Gronwall's paper, the quadratic to be solved is his Eq. (18). In carrying through the treatment in the notation of this article, we would let $\rho_n=1-R_1R_n$; then Gronwall's (18) becomes

$$\rho+T_1^2/\rho=\rho_1+T_1^2$$

$$R=(1/2R_1)(1-T_1^2+R_1^2-[(1+T_1^2-R_1^2)^2-4T_1^2]^{\frac{1}{2}}) \quad (3)$$

It is interesting to note that this same result was obtained with a slightly different method of approach by Darwin[8], though it is not explicitly stated in his paper in exactly this form. With Darwin let t_n be the amplitude of the total transmitted wave above the $(n+1)$st plane. Then t_0 is the amplitude of the incident beam. If r_n is the amplitude of the total reflected wave above the $(n+1)$st plane, then r_0 is that of the reflected beam from an infinite number of planes. As before let R_1 and T_1 be the amplitudes of the waves reflected and transmitted by a single plane. Then it follows that

$$r_n=R_1t_n+T_1r_{n+1} \quad (4)$$

$$t_{n+1}=T_1t_n+R_1r_{n+1} \quad (5)$$

If we eliminate r from these equations, we obtain

$$T_1(t_{n-1}+t_{n+1})=t_n(1+T_1^2-R_1^2) \quad (6)$$

Darwin now assumes a solution of the form

$$t_n=t_0x^n \quad (7)$$

Solving for x after insertion in (6) gives

$$2T_1x=1+T_1^2-R_1^2\pm[(1+T_1^2-R_1^2)^2-4T_1^2]^{\frac{1}{2}} \quad (8)$$

in which it is easily shown[9] that the negative sign alone gives a result of physical significance.

From (7) and Eqs. (4) and (5) we may also obtain

$$(r_0/t_0)=(1/2R_1)(2R_1^2+2T_1x-2T_1^2) \quad (9)$$

and if we substitute the correct value of x from (8)

$$r_0/t_0=(1/2R_1)(1-T_1^2+R_1^2-[(1+T_1^2-R_1^2)^2-4T_1^2]^{\frac{1}{2}}) \quad (10)$$

This is the result of Gronwall and Lamson if we consider t_0 as unity. The method of Darwin thus involves only first order difference equations, but Gronwall's method seems more readily adaptable to the study of reflec-

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Now the product of the roots of this equation (solved for ρ), is T_1^2 and if they are unequal, one is greater and one less than T_1. But from our equation (2), the present ρ_n must be greater than T_1 or the amplitude of the transmitted beam would increase in the passage through the system. Thus the larger value of ρ is the physically significant one, as Gronwall concludes from other considerations.

[8] Darwin, Phil. Mag. **27**, 675, see p. 678 (1914).

[9] From the form of the quadratic from which (8) is obtained it follows that the product of the two roots given in (8) must be unity. If they are unequal, only the one less than unity can have physical significance by (7).

tion and transmission by a finite number of planes. Thus we see that three different methods of approach lead to the same solution, as expressed in (3).

If we consider the expression (3) for the amplitude of the reflected beam, we see that for a certain range of R_1 and T_1, namely $T_1<1-R_1$. R will be imaginary. The physical significance of this is of course that there is a phase shift in reflection, and that

$$I=|R|^2 \tag{11}$$

where I is the intensity of the reflected beam.

Let us assume that the wave trains incident on, and reflected and transmitted by, a single plane, may be represented as follows.

$$y_i=\epsilon^{i\omega t} \tag{12}$$

$$y_r=b\epsilon^{i(\omega t+\delta)} \tag{13}$$

$$y_t=k\epsilon^{i\omega t} \tag{14}$$

Thus in (13) we assume a phase shift δ on reflection, but in (14) we neglect the shift in transmission. From these assumptions it follows that

$$R_1=b\epsilon^{i\delta},\quad T_1=k \tag{15}$$

If we substitute these values in (3) and perform the operation indicated in (11) we should obtain an expression for the reflected intensity. Even with the simple assumptions (12), (13), (14), this expression becomes very complicated if the operations are carried out without auxiliary assumptions. We will first assume that δ is small so that $\epsilon^{i\delta}=1+i\delta$. We will also set $k=1-h$. Using these substitutions it follows, without neglecting any terms, that

$$\begin{aligned}[(1-R_1^2+T_1^2)^2-4T_1^2]^{\frac{1}{2}}=[&b^4-4b^2+2b^2h(2-h)\\&+h^2(2-h)^2-i\delta(8b^2-4b^4-4b^2h(2-h))]^{\frac{1}{2}}.\end{aligned} \tag{16}$$

If h and b are small, and terms of power higher than two may be neglected in comparison with $\pm(h^2-b^2)$, this may be written

$$[(1-R_1^2+T_1^2)^2-4T_1^2]^{\frac{1}{2}}=2[(h^2-b^2)-2b^2i\delta]^{\frac{1}{2}} \tag{17}$$

We may express the result of taking the square root in (17) in two ways

$$\text{Case I}\quad h>b\quad 2((h^2-b^2)^{\frac{1}{2}}-b^2i\delta(h^2-b^2)^{-\frac{1}{2}}) \tag{18}$$

$$\text{Case II}\quad h<b\quad 2(-b^2\delta(b^2-h^2)^{-\frac{1}{2}}+i(b^2-h^2)^{\frac{1}{2}}) \tag{19}$$

In obtaining these expressions expansion by the binomial theorem was used, neglecting higher order terms.

If we treat first Case I, and insert (18) as the value of the radical in (3), we obtain, setting $k^2=1-2h$

$$R=(1/2b)\{2h+b^2-2(h^2-b^2)^{\frac{1}{2}}+2b^2\delta^2(h^2-b^2)^{-\frac{1}{2}} - i\delta(2h-b^2-2(h^2-b^2)^{\frac{1}{2}}-2b^2(h^2-b^2)^{-\frac{1}{2}}\} \quad (20)$$

Now if δ is small, the real part of R will be much greater than the imaginary part, and we obtain

$$I=(1/b^2)(h-(h^2-b^2)^{\frac{1}{2}})^2=(h/b-[(h^2/b^2)-1]^{\frac{1}{2}})^2 \quad (21)$$

In Case II, we obtain for R

$$R=(1/2b)\{2h+b^2+2b^2\delta(b^2-h^2)^{-\frac{1}{2}}-2\delta(b^2-h^2)^{\frac{1}{2}} - i(2h\delta-b^2\delta+2b^2\delta^2(b^2-h^2)^{\frac{1}{2}}+2(b^2-h^2)^{\frac{1}{2}}\} \quad (22)$$

Neglecting higher order terms, this gives

$$R=(1/2b)(2h-2i(b^2-h^2)^{\frac{1}{2}}) \text{ and } I=1 \quad (23)$$

Thus in Case II the intensity of the reflected beam will differ from that of the incident only by very small quantities. This means practically 100% reflection under the ideal conditions postulated.

Neither of the results (22) or (23) are valid if h and b are so nearly equal that terms in their cubes and higher powers are not negligible in comparison with $\pm(h^2-b^2)$. Nevertheless it is possible to evaluate I if $h=b$, thus obtaining a point in this region. It is easily shown that here the intensity of reflection, as in Case II, will differ from unity only by very small quantities.

Case II, $b>h$, is the most important, as at the wave-lengths ordinarily used, the crystals widely used in x-ray spectroscopy have $b>h$. The result of perfect reflection from a perfect crystal at the maximum of the "rocking curve" for this case has previously been obtained by Darwin and Ewald. The result of Case I, $b<h$, might possibly be of interest in the reflection of very soft x-rays from crystals containing heavy atoms.

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SPARK SPECTRUM OF COPPER (Cu II)

By A. G. Shenstone

Abstract

Terms in the spectrum of Cu(II.).—The spark spectrum of copper consists of (1) a low set of terms ^3D and ^1D from the structure (d^9s); (2) an intermediate set ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F (d^9p); (3) a high set ^3D, ^1D (d^9, s); (4) probably a ^1S (d^{10}), the lowest term and giving combinations outside the observed range. All of these terms except ^1S have been identified by intensities of combinations and by Zeeman effects. They are all inverted except ^3F which is only partially so; and the interval rule does not hold. The terms $^3D_3'$ and $^1F_3$ apparently share their g-sum and are otherwise not differentiable. The value of ^1S can be found from arc spectrum limits to be about 22224 wave numbers lower than $^3D_3$. The application of the combination principle makes possible the calculation of accurate wave numbers in the ultra-violet to λ1944.

Comparison with corresponding terms in Ni(I) and Pd (I).—A comparison is made with corresponding terms in Ni(I) and Pd(I) and it is shown that the limits of the component term series in all three cases apparently do not agree with Hund's predictions. It is important that the difference $^3D_3-{}^3D_1$ in the three spectra is constant within the series to less than 1/10%; in the case of Cu(II), being apparently absolutely constant and equal to the difference $^4D_4-{}^4D_1$ of the arc spectrum.

An ionization potential for Cu(II) is calculated as about 20.5 volts.

IN AGREEMENT with the theory of the production of spectra developed by Hund[1] the author has shown in a recent paper[2] that the arc spectrum of copper consists of two parts; first, an ordinary doublet spectrum due to the atom in states in which all but one of the twenty-nine electrons are in closed groups of orbits; second, a quartet-doublet spectrum due to the atom in states in which nine of the last eleven electrons are in 3_3 orbits, one is in a 4_1 orbit and the last is in either a 4_1 or some less firmly bound condition. There are indications of a less completely developed third spectrum arising from structures in which only eight electrons remain in 3_3 orbits. The lowest terms of the first two types of spectra are $1^2S(d^{10}s)$ and $m^2D(d^9s^2)$. The brackets give, symbolically, the electron configurations, the letters denoting the k-values of the orbits, and the indices the numbers of electrons. Only the last eleven electrons are given, since the others remain in closed groups.

The two types of ion on which the two branches of the arc spectrum are built are (d^{10}) and (d^9s) which spectroscopically are terms of type ^1S and ^3D, ^1D. The series of terms in the two branches of the arc

[1] Hund, Zeits. f. Physik, **33**, 841 (1925).
[2] Shenstone, Phys. Rev. **28**, 449 (1926).

spectrum will, therefore, have as limits the spark ^1S and the various components of the terms ^3D, ^1D. We can, then, find approximately the difference $^1S-^3D$ by calculating the limits of series of terms in the two parts of the arc spectrum. The limit of the ^2S terms is taken as zero, according to the usual convention. There are two ^4D terms (d^9s, s) available for the calculation of the limits of the second arc spectrum. The $^4D_4$ terms are the lowest and should converge to the spark $^3D_3$. This limit falls at -22224, indicating that the difference $^1S-^3D_3=22224$, the ^1S being the lower term. This value may be in error by perhaps 1500 units since only two series members are available for the calculation.

Combining with the low spark terms ^1S and ^3D, ^1D there should be found a triad ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F due to the electron configuration d^9p. Such terms should also combine with higher series members of the sequence ^3D, ^1D, (d^9, s). The comma between d and s is used to denote that the s-electron is in an excited level, for instance 5_1, 6_1, etc.

The spectrum of the copper arc in the ultra-violet contains many strong spark lines which can be distinguished with some difficulty by the ordinary arc-spark comparison method. If the arc is run from batteries and self-induction is avoided as far as possible, the spark lines become relatively weak and the distinction can be made more easily. The low-voltage arc[3] in Cu vapor has also been used by the author for the separation of arc and spark lines.

A number of the ultra-violet spark lines have been observed by Stücklen[4] in the under-water spark and wrongly placed as arc lines. From their appearance under the conditions of that experiment, there can be no doubt that they are among the most easily excited spark lines. They are all included in the following Table I which gives the combinations of the lowest ^3D, ^1D with the intermediate terms ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F. It will be noticed that all of the terms of Table I are inverted with the exception of the partially-inverted ^3F, in agreement with the predictions of the Hund theory. The method of determining the designations of the terms and their magnitudes is given below.

The lowest term of this set is $^3D_3$ and it has been arbitrarily assigned the value zero, the remaining terms then all assuming positive values. The assignment is provisional only, awaiting the discovery of the exact difference $^1S-^3D_3$ which would then be added to all of the terms.

The combinations of the intermediate set of terms of Table I with a higher ^3D, ^1D are given in Table II. These two sets include every copper spark line of the quartz region which is also emitted in the ordinary copper arc. A large number of the lines also appear in the spectrum of the low-voltage arc when the current density is large.

[3] Shenstone, Phil. Mag. **49**, 952 (1925).
[4] Stücklen, Zeits. f. Physik **34**, 562 (1925).

The lines of Table II lie, for the most part, in a spectral region in which greater accuracy of measurement is possible. The term differences have, therefore, been computed from that table. The actual values of terms above $^3D_3$ have then been computed by the use of the few lines of Table I which have been measured with reasonable accuracy by Mitra[5] and by Wolfsohn.[6] The wave numbers of lines calculated from Hasbach's[7] and Eder's[8] measurements diverge progressively from the values predicted by the combination principle. If these differences

TABLE I

Classification of certain ultra-violet spark lines of copper.

		a^3D_3 0.0	a^3D_2 918.5	a^3D_1 2069.7	a^1D_2 4335.7
		(10)	(5)	(2)	(7)
a^3P_2	44489.9	44489.9 (W)	43571.4 (W).	42420.6	40154.3
	1497.9		(8)	(5)	(2)
a^3P_1	45987.8		45069.3 (W)	43918.1 (WM)	41652.2
	933.4			(5)	
a^3P_0	46921.2			44852.4	
		(10)			
a^3F_4	46802.1	46803.6			
	−283.0	(4)	(10)		(6)
a^3F_3	46519.1	46520.1	45601.3		42183.1
	1420.2	(3)	(4)	(8)	(0)
a^3F_2	47939.3	47941.2	47020.7 (M)	45870.4	43603.4
		(8)			(9)
a^3D_3'	48912.5	48914.8			44576.8 (WM)
	652.4	(1)	(8)	(3)	(7)
a^3D_2'	49564.9	49568.1	48648.9	47497.2	45229.4 (W)
	1608.4		(2)	(7)	(4)
a^3D_1'	51173.3		50258.6	49106.3	46838.0
		(7)	(6)		(6)
a^1F_3	49991.3	49995.0	49075.5		45655.5 (M)
		(2)	(2)	(5)	(5)
a^1D_2'	51424.3	51427.1	50509.4	49357.9	47090.2
			(1)	(1)	(5)
a^1P_1	51667.1		50751.9	49600.8	47331.1 (M)

are plotted against wave-length, a curve is obtained which rises to a maximum of about $\Delta\nu = 3.8$ at $\lambda = 2000$ and thereafter falls with shorter wave-length. If the present analysis of the Cu spark spectrum is admitted as correct, then it is possible to calculate much more accurate wave-lengths than have been previously known in the region λ1944 to λ2200. The values given in Tables I and II are Hasbach's and Eder's; the values in the Table IV at the end of this paper are those calculated by the use of the combination principle. The frequencies given in Table IV have a probable error of about 0.4 units.

[5] Mitra, Ann. d. physique **19**, 315 (1923).
[6] Wolfsohn, Ann. d. Physik **80**, 415 (1926).
[7] Hasbach, Zeits. f. Wiss. Phot. **13**, 399 (1914).
[8] Eder, Wien. Ber. **123** II a, 616 (1914).

The intensities given in Tables I and II are the author's visual estimates of the photographic intensities of the lines. In general, the combinations which do not involve a change in multiplicity are in excellent agreement with theoretical expectation, with one striking exception, the absence of the line $a^3D_2-a^3D_3'$. Its intensity should be about 4; and, indeed, the corresponding line of Table II is present with

TABLE II

Classification of additional spark lines of copper.

		b^3D_3 86083.7	b^3D_2 86404.6	b^3D_1 88153.3	b^1D_2 88435.0
		(5)	(0)		(0)
a^3P_2	44489.9	41593.8	41914.7		43945.1
	1497.9		(5)	(0)	(0)
a^3P_1	45987.8		40416.8	42165.5	42447.3
	933.4			(1)	
a^3P_0	46921.2			41232.1	
		(10)			
a^3F_4	46802.1	39281.6			
	−283.0	(4)	(8)		(0)
a^3F_3	46519.1	39564.9	39885.5		41915.5
	1420.2	(0)	(5)	(6)	(1)
a^3F_2	47939.3	38145.2	38465.4	40213.9	40496.9
		(7)	(3)		(6)
a^3D_3'	48912.5	37171.2	37492.1		39521.4
	652.4	(1)	(7)	(4)	(0)
a^3D_2'	49564.9	36518.9	36839.7	38588.4	38870.0
	1608.4		(4)	(6)	
a^3D_1'	51173.3		35231.2	36980.2	
		(6)	(5)		(6)
a^1F_3	49991.3	36092.4	36413.4		38443.7
		(1)	(0)	(5)	(7)
a^1D_2'	51424.3	34659.5	34980.5	36729.0	37010.7
			(5)	(1)	(6)
a^1P_1	51667.1		34737.5	36486.9	36767.9

intensity 3. The intensities of the intersystem combination lines do not obey, even approximately, the usual qualitative rules. For instance, a^1D_2 combines with a^3P_2 much more strongly than with a^3P_1. Moreover, the relative intensities of the intersystem lines of Tables I and II are entirely different. This seems quite anomalous.

ZEEMAN EFFECTS

Zeeman patterns of most of the lines included in Tables I and II have been measured. The magnet used produced a field of about 34000 gauss, and the lines were photographed in a Hilger E1 quartz spectrograph. In the region below λ2500 the dispersion is great enough to give trustworthy measurements of Zeeman separations; but, in the

longer wave-lengths a rather large error may occur. The patterns, except in a few cases, are resolved only as triplets. In such cases the pattern predicted by the use of Landé's g-values has been reduced to a theoretical blend triplet by the following procedure. The intensities of the components of a complicated pattern follow a quadratic formula and in consequence the center of gravity will always be approximately 1/4 of the way from the strongest to the weakest component. For instance,

$$^3D_3-{}^3P_2 \text{ Z.E.} = (\bar{0},1,2)\bar{6},7,8,9,10\ /6\sim(0)7/6\sim(0)1.17.$$

I am indebted to Professor H. N. Russell for this useful suggestion.

The observed patterns and the calculated are both given in the wave-length Table IV at the end of this paper. The agreement is very good in the main and fixes without doubt the nature of the low ^3D, ^1D terms. In fact, all the lines of Table I show excellent agreement except those involving the terms a^3D_3' and a^1F_3. These two terms certainly have g-values which are neither 1 nor 4/3, the theoretical values. The observed patterns are, however, consistent with the sharing of the g-sum 7/3 between the two terms, the g of a^3D_3' being approximately 1.1 and of a^1F_3 approximately 1.2. From relative intensities of combinations, these two terms are also interchangeable. It is, therefore, impossible to differentiate between them and the designations given rest solely on their positions relative to the other terms a^3D_2 and a^3D_1. A parallel case occurs in the Cu arc spectrum, where a^4D_3' and a^2F_3 are apparently not differentiable.

The Zeeman patterns of the lines of Table II are satisfactory considering the smallness of the actual separations on the plates. They again show disagreement for the terms a^3D_3' and a^1F_3 discussed above. In Table IV the asterisks indicate those lines which involve the two terms in question.

There remain only comparatively weak lines of Cu(II) unclassified. A number of these are undoubtedly due to structures such as d^9d combining with d^9p. A number of individual levels have been found, but the lines are so weak and so poorly measured that in no case can the levels be classified with certainty. This material is therefore reserved for future publication.

The lowest term of the copper spark should be $^1S(d^{10})$. As has been pointed out above, it should lie about 22224 wave-numbers deeper than a^3D_3. The possible combinations are contained in $d^9p\rightarrow d^{10}$ and reduce to the following three only, because of the j-selection principle. They should lie within 1500 wave-numbers of the following positions.

$^1S-a^3P_1$	$\nu=68212$	$\lambda=1466$
$^1S-a^3D_1$	$\nu=73397$	$\lambda=1363$
$^1S-a^1P_1$	$\nu=73891$	$\lambda=1353$

Of these strong lines, the last should be the most intense.

One of the lowest states of the doubly ionized copper atom Cu III should be a ^2D term which arises from the structure d^9. The addition of an s-electron gives terms ^3D, ^1D (d^9s) which are undoubtedly the low terms of Table I and the high terms of Table II. The addition of a second s-electron yields terms ^4D, ^2D, $^2D(d^9s, s)$; or, when the two s-electrons both occupy 4_1 orbits (d^9s^2), a ^2D alone. Such terms are the c^4D, e^4D and m^2D of the atomic spectrum. It can be shown[9] that the series of component terms of $^4D(d^9s, s)$ should converge to different components of the spark ^3D term. In particular, the series $^4D_4$ should converge to $^3D_3$ and $^4D_1$ to $^3D_1$. In other words, the difference $^4D_4-{}^4D_1$ should approach, at any rate in higher series members, the difference $^3D_3-{}^3D_1$. The following table shows that in fact this difference $^4D_4-{}^4D_1$ is already in the first series member practically equal to $^3D_3-{}^3D_1$. The evidence is very strong that the same difference also persists into the spectrum Cu III where it should be $^2D_3-{}^2D_2(d^9)$.

Cu(I)	d^9s^2	$m^2D_3-m^2D_2=2042.9$	Cu(II)	d^9s	$a^3D_3-a^3D_1=2069.7$
	d^9s,s	$c^4D_4-c^4D_1=2069.0$		d^9,s	$b^3D_3-b^3D_1=2069.6$
	d^9s,s	$e^4D_4-e^4D_1=2069.6$	Cu(III)	d^9	$^2D_3-{}^2D_2=2069.6?$

The remarkable agreement of the separations in this case and of the similar terms in the spectra of Ni(I) and Pd(I) given below, is predicted by the theory recently outlined by Slater.[10]

The following approximate agreements of arc and spark separations are also significant. The arc terms belong to the group which arises from the structure $d^9s\ d$; the spark term is the lowest ^3D.

Cu(I)	$d^4G_6-d^4G_5=848.1$	$d^4G_5-d^4G_3=1220.0$
	$d^4F_5-d^4F_4=802.6$	$d^4F_4-d^4F_2=1223.4$
	$d^4D_4-d^4D_3=798.8$	
	$d^4P_3-d^4P_2=749.0$	
Cu(II)	$a^3D_3-a^3D_2=918.5$	$a^3D_2-a^3D_1=1151.2$

The ^4G term used above is the alternative given in the author's paper[2] at the foot of page 459.

In addition to the above excellent agreement of separations, there is the fact that $^4G_4-{}^4G_3$, $^4F_3-{}^4F_2$, $^4P_2-{}^4P_1$ are all small, fulfilling the theoretical prediction that each of these pairs of terms should have a single limit. For bringing to my notice all the above agreements of separation and for the prediction from them of the spark intervals I am indebted to O. Laporte.

The spectra of Ni(I) and Pd(I) should be similar to that of Cu(II). Pd(I) does in fact possess two sets of terms corresponding in detail to the high and low ^3D, ^1D sets in Cu(II). The first set is as given by

[9] Hund, Zeits. f. Physik **34**, 296 (1925).
[10] Slater, Phys. Rev. **28**, 291 (1926).

TABLE III

Corresponding terms in spectra of Cu(II), Ni(I) and Pd(I). Series limits and ionization potentials.

	j	Cu(II) Terms	$\Delta\nu$	$\Delta\nu$(sum)	Ni(I) Terms	$\Delta\nu$	$\Delta\nu$ (sum)	Pd(I) Terms	$\Delta\nu$	$\Delta\nu$(sum)
^3D	3	0.0			204.8			6564.0		
			918.5			675.0			1191.0	
(d^9s)	2	918.5		2069.7	879.8		1508.3	7755.0		3529.9
			1151.2			833.3			2338.9	
	1	2069.7			1713.1			10093.9		
			2266.0			1696.8			1627.8	
^1D	2	4335.7			3409.9			11721.7		
^3D	3	86083.7			42605.8			48804.2		
			320.9			184.1			215.3	
(d^9, s)	2	86404.6		2069.6	42789.9		1506.3	49019.5		3532.1
			1748.7			1322.2			3316.8	
	1	88153.3			44112.1			52336.3		
			281.7			150.4			151.4	
^1D	2	88435.0			44262.5			52487.7		
Limits of		Cu(III) (d^9)			Ni(II) (d^9)			Pd(II) (d^9)		
^3D	3	144388		$^2D_3$	62944		$^2D_3$	69106		$^2D_3$
	2	144502		2069	63017		1505	69099		3533
	1	146457		$^2D_2$	64449		$^2D_2$	72639		$^2D_2$
^1D	2	146048			64247			72452		
Ionization potentials		17.8 volts			7.8 volts			8.5 volts		

McLennan and Smith[11]; but, in the high set the $^3D_2$ and $^1D_2$ have been interchanged. In the above paper this set of levels is arranged so that ^3D is partially inverted, though the intensity relations agree equally well with the present arrangement. Moreover, it is now brought into perfect accord with the similar terms in both Cu(II) and Ni(I). The two sets of ^3D, ^1D of Ni(I) are contained in Bechert and Sommer's[12] paper. They were picked as members of a series by Hund.[1]

The corresponding terms of the three spectra are given opposite each other in Table III. The most striking similarity is found in the interval $^3D_3-{}^3D_1$. In Cu(II), this interval changes when we pass from the low ^3D to the high ^3D, by only 0.1 wave-numbers, a change which is quite within the experimental error. In Ni(I) the corresponding change is -2.0 and in Pd(I), $+2.2$ wave-numbers. The $^3D_2$ and $^1D_2$ terms are placed in relatively the same positions in all three spectra. The ^3D intervals are all reversed from the 'normal' order, i.e., $^3D_3-{}^3D_2 < {}^3D_2-{}^3D_1$.

The series of component levels of ^3D and $^1D(d^9s)$ must converge to the two components of the term $^2D(d^9)$ of the next higher ion. It can be shown (Hund[9]) that the limits should be as follows: $^3D_3$ and $^1D_2$ converge to $^2D_3$; and $^3D_2$ and $^3D_1$ to $^2D_2$.

At the foot of Table III are given the series limits calculated from the two sets of levels for each of the three spectra. The ionization potentials are obtained from the $^3D_3$ limits. In the case of Cu II the potential given is for the removal of the *s*-electron from the structure d^9s. The ionization from d^{10} to d^9 would require approximately 20.5 volts, the difference of 2.7 volts being calculated from the term difference $^1S-{}^3D_3$.

It has been pointed out that the extreme separation of the ^3D terms ($^3D_3-{}^3D_1$) is almost constant in each of the spectra. This fact, and the behavior of the extreme terms in analogous cases in other spectra, makes possible a reasonable certainty that the separation of the calculated limits for these levels will agree closely with the actual separation. For example, the analogous ^4D terms in Cu(I) give almost exact agreement of calculated and experimental limit separations.

The calculation of limits from only two series members in such cases as $^3D_2$ and $^1D_2$ must necessarily give much less certain results, and conclusions drawn from such calculations must require confirmation. An extreme case is the series of ms^3P terms in lead.[13] Nevertheless, there is a peculiarity of the calculated limits in these three spectra which is at least noteworthy. That is, the exact agreement of the calculated limits for the component series $^3D_3$ and $^3D_2$; and the only slightly less

[11] McLennan and Smith, Roy. Soc. Proc. **112A**, 110 (1926).
[12] Bechert and Sommer, Ann. d. Physik **77**, 351 (1925).
[13] Gieseler and Grotrian, Zeits. f. Physik **39**, 377 (1926).

TABLE IV

Wave-lengths and classification of spark lines of Cu.

λ	Auth.	Int.	ν	Comb.	Z. E. (obs.)	Z. E. (calc.) Blend
2884.38	H	1	34659.5	$a^1D_2' - b^3D_3$		
2877.89	H	5	34737.5	$a^1P_1 - b^3D_2$	(0)1.19	(0)1.25
2857.9	Ex	0	34980.5	$a^1D_2' - b^3D_2$		
2837.56	H	4	35231.2	$a^3D_1' - b^3D_2$	(0)1.48	(0)1.5
2769.85	H	6	36092.4	$a^1F_3 - b^3D_3$	(0)1.22	(.84)1.16*
2745.43	H	5	36413.4	$a^1F_3 - b^3D_2$	(0)1:31	(0) .83*
2739.9	Ex	1	36486.9	$a^1P_1 - b^3D_1$		
2737.5	Ex	1	36518.9	$a^3D_3' - b^3D_3$		
2721.84	H	5	36729.0	$a^1D_2' - b^3D_1$	(0)1.31	(0)1.25
2718.96	H	6	36767.9	$a^1P_1 - b^1D_2$	(0)1.04	(0)1.00
2713.66	H	7	36839.7	$a^3D_2' - b^3D_2$	(0)1.02	(0)1.17
2703.34	H	6	36980.2	$a^3D_1' - b^3D_1$	(0) .47	(0) .50
2701.12	H	7	37010.7	$a^1D_2' - b^1D_2$	(0)1.02	(0)1.00
2689.46	H	7	37171.2	$a^3D_3' - b^3D_3$	(.57)1.17	(0)1.33*
2666.44	H	3	37492.1	$a^3D_3' - b^3D_2$	(0) .99	(0)1.50*
2620.78	Ex	0	38145.2	$a^3F_2 - b^3D_3$		
2600.43	H	6	38443.7	$a^1F_3 - b^1D_2$	(0)1.30	(0)1.00*
2598.96	H	5	38465.4	$a^3F_2 - b^3D_2$	(.82) .89	(.87) .92
2590.68	H	4	38588.4	$a^3D_2' - b^3D_1$	(0)1.40	(0)1.50
2571.91	H	0	38870.0	$a^3D_3' - b^1D_2$		
2544.96	H	10	39281.6	$a^3F_4 - b^3D_3$	(0)1.11	(0)1.13
2529.48	H	6	39521.9	$a^3D_3' - b^1D_2$	(0)1.03	(0)1.66*
2526.73	H	4	39565.0	$a^3F_3 - b^3D_3$	(.67)1.12	(.62)1.21
2506.41	H	8	39885.5	$a^3F_3 - b^3D_2$	(0) .98	(0)1.00
2489.64	H	7	40154.3	$a^1D_2 - a^3P_2$	(.86)1.21	(.75)1.25
2485.95	H	6	40213.9	$a^3F_2 - b^3D_1$	(0) .72	(0) .75

λ	Auth.	Int.	ν	Comb.	Z. E. (obs.)	Z. E. (calc.) Blend
2473.47	H	5	40416.8	$a^3P_1 - b^3D_2$	(0) .83	(0)1.0
2468.58	H	1	40496.9	$a^3F_2 - b^1D_2$		
2424.56	H	1	41232.0	$a^3P_0 - b^3D_1$		
2403.47	H	4	41593.8	$a^3P_2 - b^3D_3$	(0)1.08	(0)1.17
2400.10	H	2	41652.2	$a^1D_2 - a^3P_1$	(0) .64	(0) .75
2385.06	H	0	41914.8	$a^3P_2 - b^3D_2$		
			5.5	$a^3F_3 - b^1D_2$		
2370.88	H	0	42165.5	$a^3P_1 - b^3D_1$		
2369.88	H	6	42183.3	$a^1D_2 - a^3F_3$	(0)1.12	(0)1.17
2356.65	Calc	2	42420.2	$a^3D_1 - a^3P_2$	$(\bar{0}, .9)1.45, \bar{2}.\overline{49}$	$\frac{(\bar{0}, 2)1, 3, \bar{5}}{2}$
2355.15	"	0	42447.2	$a^3P_1 - b^1D_2$		
2294.374	W	5	43571.4	$a^3D_2 - a^3P_2$	(.66)1.37	(.59)1.33
2292.68	Calc	0	43603.6	$a^1D_2 - a^3F_2$		
2276.261	W.M	5	43918.1	$a^3D_1 - a^3P_1$	(1.0).48, 1.52	$\frac{(2)1, 3}{2}$
2274.86	Calc	0	43945.1	$a^3P_2 - b^1D_2$		
2247.003	W	10	44489.9	$a^3D_3 - a^3P_2$	(0)1.15	(0)1.17
2242.621	W.M	9	44576.8	$a^1D_2 - a^3D_3'$	(0)1.16	(0)1.66*
2228.88	Calc	5	44851.5	$a^3D_1 - a^3P_0$	(0) .49	(0).50
2218.107	M	8	45069.4	$a^3D_2 - a^3P_1$	(0) .86	(0)1.00
2210.27	Calc	7	45229.2	$a^1D_2 - a^3D_2'$	(0) .96	(0)1.04
2192.27	"	10	45600.6	$a^3D_2 - a^3F_3$	(0) .96	(0)1.00
2189.631	M	6	45655.6	$a^1D_2 - a^1F_3$	(0)1.50	(0)1.00*
2179.41	Calc	8	45869.6	$a^3D_1 - a^3F_2$	(0) .80	(0) .75
2148.98	"	4	46519.1	$a^3D_3 - a^3F_3$	(.79)1.16	(.63)1.21
2135.98	"	10	46802.1	$a^3D_3 - a^3F_4$	(0)1.08	(0)1.12
2134.36	"	4	46837.6	$a^1D_2 - a^3D_1'$	(0)1.11?	(0)1.25

λ	Auth.	Int.	ν	Comb.	Z. E. (obs.)	Z. E. (calc.) Blend
2125.047	M	4	47020.8	$a^3D_2-a^3F_2$	(.82) .89	(.88) .92
2122.98	Calc	5	47088.6	$a^1D_2-a^1D_2'$	(0)1.05	(0)1.00
2112.09	"	5	47331.4	$a^1D_2-a^1P_1$	(0)1.02	(0)1.00
2104.81	"	3	47495.0	$a^3D_1-a^3D_2'$	(0)1.34	(0)1.5
2085.30	"	3	47939.3	$a^3D_2-a^3F_3$	(0)2.37†	(0)2.0
2054.99	"	8	48646.4	$a^3D_2-a^3D_2'$	(0)1.09	(0)1.17
2043.81	"	8	48912.5	$a^3D_3-a^3D_3'$	(.60)1.06	(0)1.33*
2037.13	"	6	49072.8	$a^3D_2-a^1F_3$	(0)1.22	(0) .84*
2035.85	"	7	49103.6	$a^3D_1-a^3D_1'$	(0) .48	(0) .50
2025.50	"	5	49354.6	$a^3D_1-a^1D_2'$	(0)1.29	(0)1.25
2016.90	"	1	49564.9	$a^3D_3-a^3D_3'$		
2015.58	"	1	49597.4	$a^3D_1-a^1P_1$		
λ (Vac)						
2000.348	"	7	49991.3	$a^3D_3-a^1F_3$	(0)1.08	(.84)1.16*
1989.860	"	2	50254.8	$a^3D_2-a^3D_1'$		
1979.971	"	2	50505.8	$a^3D_2-a^1D_2'$	(0)1.01	(.25)1.08
1970.497	"	0	50748.6	$a^3D_2-a^1P_1$		
1944.606	"	2	51424.3	$a^3D_4-a^1D_2'$		

† Outside of wide pattern.
* Lines involving a^3D_3' or a^1F_3.
H—Hasbach, Kayser & Konen. Vol. VII.
Ex—Exner and Haschek, " " "
M—Mitra, Ann. d. physique **19**, 315 (1923).
W—Wolfsohn, Ann. d. physik **80**, 415 (1926).

exact agreement for $^3D_1$ and $^1D_2$, contrary to the theory. The following diagram compares the theoretical prediction and the apparent result.

Theoretical limits	Apparent limits
$^3D_3, {}^1D_2 \rightarrow {}^2D_3$	$^3D_3, {}^3D_2 \rightarrow {}^2D_3$
$^3D_2, {}^3D_1 \rightarrow {}^2D_2$	$^3D_1, {}^1D_2 \rightarrow {}^3D_2$

It is remarkable that the apparent limits of $^3D_2$ and $^1D_2$ are exactly reversed from their expected positions, i.e., the deviations from the theoretical positions are closely $\mp(^2D_3-{}^2D_2)$. In other words, there would be excellent agreement if the designations of $^3D_2$ and $^1D_2$ could be interchanged. This, however, is definitely prohibited by Zeeman effects and intensities of combinations in Cu II, and, therefore, by analogy, in the other spectra.

The same type of peculiarity of convergence is evident in the following case of the ^4D terms of Cu(I). The limits of the extreme terms agree exactly with the experimental limits. The $^4D_2$ term, however, instead of converging with $^4D_1$ to $^3D_1$ diverges apparently to $^3D_2$, as is evident from the separations given.

Limits		Δν		Δν
$^4D_4$	22224			
		899	$^3D_3$	918
$^4D_3$	22428		$^3D_2$	
				1151
$^4D_2$	23123	1170	$^3D_1$	
$^4D_1$	24293			

Such peculiarities may be coincidence. They would then be merely evidence of the same disturbing forces in all three spectra. This would not be surprising, since the structures involved are the same. The discovery of higher series members should remove any doubt there may be in the interpretation of these points.

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ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES

III. INTENSITY RELATIONS

By Robert S. Mulliken

Abstract

The correspondence principle predicts definite intensity relations for P, Q and R band lines in molecules having a rotational energy term $F(j) = B(j^2-\sigma^2)+\ldots$, provided σ is an electronic quantum number correlated with a precession about the internuclear axis (along which the angular momentum $\sigma h/2\pi$ is directed). Hönl and London have used the summation rule method to obtain exact equations for each of three possible cases $\Delta\sigma=0, \pm1$; these equations are recast here in more convenient form. According to recent work of Dennison, these equations very probably remain valid in the new quantum mechanics. Theoretical curves for the cases $\Delta\sigma=+1$ and -1 are given.

Various electronic emission bands have been interpreted by the writer as corresponding to electronic transitions $^1S\rightarrow{}^1S$(CuH type), $^1P\rightarrow{}^1S$(AlH, He_2 "series" bands), $^1D\rightarrow{}^1P$ (He_2 λ5733), $^1S\rightarrow{}^1P$(He_2 λ4546, λ6400, and CO Ångstrom bands), with $\sigma=0$ for ^1S, $\sigma=1$ for ^1P, and $\sigma=2$ for ^1D states. Comparison of the predictions of the above theory with the available intensity data on the bands mentioned, assuming in each case thermal equilibrium at a suitable (arbitrarily chosen) temperature, gives in every case qualitative agreement with the predicted distribution for that particular case; usually the agreement appears to be complete within the often comparatively large uncertainties of the data. Oscillation-rotation absorption bands corresponding to $\sigma'=\sigma''=0$ fall under the theory as a special case, and the data on these bands (in particular the quantitative data of Kemble and Bourgin on HCl) agree with the theory. Intensity relations in $^2S\rightarrow{}^2S$ (violet CN type) and $^2P\rightarrow{}^2S$ (ZnH type) transitions are briefly discussed; the intensity relations resemble those for $^1S\rightarrow{}^1S$ and $^1P\rightarrow{}^1S$ transitions, but no satisfactory theory is as yet available.

The close agreement between theory and experiment for spectra interpreted as due to transitions involving ^1S, ^1P, or ^1D states seems to make conclusive the already strong evidence for these interpretations. Furthermore (in connection with the observed selection $\Delta\sigma=0, \pm1$) it shows that ^1S, ^1P, and ^1D molecular states all belong to a class in which σ is an electronic quantum number correlated with a precession about the internuclear axis.

In $^1S\rightarrow{}^1P$, $^1P\rightarrow{}^1S$, and $^1D\rightarrow{}^1P$ transitions, there exist in practice (cf. II of this series) two rotational states (A and B) for each value of j. The agreements noted were obtained by disregarding the subdivision into A and B sub-states; the fact that agreement was obtained in this way shows incidentally that the a priori probabilities of A and B sub-states must be equal.

Another phenomenon not contemplated by the theory, but present in all the He_2 bands, is that alternate lines are missing in each branch. The cause of this is obscure, but the evidence for its existence is conclusive and so justifies the procedure, which is necessary to obtain the agreement described above between theory and experiment, of inserting in Eqs. (5)–(6) a factor zero for alternate lines in each branch.

Introduction

THE importance of a study of intensity relations among band lines has been emphasized by Kratzer[1] and by Kemble[2,3]. Up to the present, however, practically nothing has been done to compare experiment with theory except in the case of bands composed of P and R branches only.

As a result of a study of evidence from missing lines, presence of Q branches, and systematic relations for odd and even molecules, the writer has recently concluded[4,5,6,7] that many known band spectra involve rotational terms of the form $B(j^2-\sigma^2)+\cdots$. Band spectra also exist which involve terms of the form $B(j-\rho)^2+\cdots$, while there are others involving more complex forms. A study of observed intensity relations lends strong support, as will be shown in the present paper, to the conclusions just mentioned. For notation, etc., reference should be made to a previous paper.[6]

Survey of Work on the Intensity Problem for Bands Containing a Single P and a Single R Branch

Bands without Q branches. Experimentally, known bands consisting of P and R branches and without Q branches comprise (*a*) infrared oscillation-rotation bands with one P and one R branch, such bands ordinarily being observed in absorption (examples: CO and halogen halide bands), (*b*) electronic bands having one P and one R branch (examples, CuH, AgH, AuH, I_2 bands), and (*c*) electronic bands having two P and two R branches, but with the two branches of each kind usually forming a series of close doublets (examples, violet CN and analogous bands).

In the case of oscillation-rotation bands, the presence of a σ is, according to the correspondence principle, a necessary and sufficient condition for the presence of a Q branch;[1,8] the presence or absence of a ρ appears to be immaterial from the standpoint of the correspondence principle. Hence for type (*a*) above, we may conclude that $\sigma=0$, $\rho\geqq 0$. (Throughout this article $\sigma h/2\pi$ and $\rho h/2\pi$ denote components of electronic angular momentum which are respectively parallel and perpendicular to the internuclear axis.) The correspondence principle then gives further information in regard to the expected intensities of the lines of the P and R branches (see below).

[1] A. Kratzer, Naturwiss. **27**, 577 (1923); Ann. d. Physik **71**, 72 (1923).
[2] E. C. Kemble, Proc. Nat. Acad. Sci. **10**, 274 (1924); Phys. Rev. **25**, 1 (1925).
[3] E. C. Kemble, Zeits. f. Physik **35**, 286 (1925).
[4] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 144 (1926).
[5] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 151 (1926).
[6] R. S. Mulliken, Phys. Rev. **28**, 481 (1926).
[7] R. S. Mulliken, Phys. Rev. **28**, 1202 (1926).
[8] A. Sommerfeld, Atombau und Spektrallinien, 4th Edition, Chapter 9, (1924).

In the case of electronic bands, the presence of a σ is a sufficient condition for the presence of a Q branch, but not a necessary one[9] unless or until restrictions are placed on the types of electronic motions which are assumed to be possible. The *absence* of a Q branch in types (b) and (c) is, however, satisfactory evidence that $\bar{\sigma}$ (i.e. σ' and σ'') is zero; but the correspondence principle gives no definite information in regard to the intensities of the P and R lines unless a molecular model is assumed.

Oscillation-rotation bands without a Q branch. By application of the correspondence principle to bands of type (a), using the device of hypothetical magnetic components to remove degeneracy, Kemble made it probable[2] that the intensities of the lines of both P and R branches should be given by the relation

$$I = ie^{-E_0/kT}, \text{ where } i = a\,\bar{p} \tag{1}$$

Here E_0 is the value of $F(j)$ for the *initial* molecular state, a is to a first approximation a constant (but see below), and $\bar{p}$ is the mean of the a priori probabilities p of the initial and final rotational states. Experimental work of Kemble and Bourgin[10] on the HCl absorption band at 3.46 μ completely confirms Eq. (1), provided $\bar{p}$ is assumed to have the values 2, 4, 6, $\cdots$ for successive lines of each branch, or what is the same thing, provided $p = 1, 3, 5, \cdots$ for the rotational states having $m = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \cdots$.

Fowler[11] and Dieke[13] have shown that Eq. (1) can also be obtained for type (a) bands by a rather formal application of the summation rule, provided the succession of p values 1, 3, 5, $\cdots$ is used, as above; any other choice of p values gives a stepwise-advancing or alternating set of intensities.

Mensing,[14] Fues,[15] and Oppenheimer[16] have shown that for oscillation-

[9] H. A. Kramers and W. Pauli, Jr. Zeits. f. Physik **13**, 351 (1923). For further discussion cf. ref. 6, p. 488.

[10] E. C. Kemble and D. G. Bourgin, Nature, June 5, 1926.

[11] R. H. Fowler, Phil. Mag. **49**, 1272 (1925). Fowler attempted to extend the application of the summation rule to the case of bands (including electronic bands) having Q branches. He concluded that the P and R branches (aside from the Boltzmann factor and variability in a) should always be equally intense here, as in bands of the simple $P-R$ type. Kemble then pointed out[3] that this conclusion based on the summation rule is in conflict with the correspondence principle, according to which there are many cases where such equality of P and R branches is not to be expected. Finally, the work of Hönl and London[12] showed that Fowler's conclusion is incorrect, and that the results of the two methods are in harmony.

[12] H. Hönl and F. London, Zeits. f. Physik **33**, 803 (1925).

[13] G H. Dieke, Zeits. f. Physik **33**, 161 (1925).

[14] L. Mensing, Zeits. f. Physik **36**, 814 (1926).

[15] E. Fues, Ann. der Physik **80**, 367 (1926).

[16] J. R. Oppenheimer, Proc. Camb. Phil. Soc. **23**, Part 3, p. 327 (1926).

rotation bands, if $j_e=0$ (i. e. $\rho=\sigma=0$),[17] the new quantum mechanics yields directly the relation $i=a\,\bar{p}$ of Eq. (1) and the p values 1, 3, 5, · · · .[18]

In a systematic study of known band spectra[6,7] the writer concluded that all known bands of types (*a*) and (*b*) are due to transitions in even molecules having $j_e'=j_e''=0$,[17] and $F(j)=Bj^2+\cdots$ with $j=m=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, · · · · Such transitions were classified as $^1S\rightarrow{}^1S$ transitions, and it was shown that definite characteristics properties ($j_e=0$, diamagnetic behavior, single rotational states) may be attributed to ^1S states, thus implying that such states correspond to a definite molecular model. It was further concluded that ^1S states belong to a class of states for which $F(j)=Bm^2+\cdots=B(j^2-\sigma^2)+\cdots$, with $\sigma=0$, 1, 2, · · · for ^1S, ^1P, ^1D, · · · states, and $j=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, · · · in all (with the condition $j\geqq\sigma$).

With $j=m=\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, · · · for ^1S states, the results of the preceding paragraphs require $p=2j$, hence Eq. (1) takes the form

$$I=ie^{-E_0/kT},\ \text{with}\ i=2aj \tag{2}$$

If $p=2j$ for ^1S states, it is reasonable to expect the same relation for ^1P, ^1D, · · · states, and in fact for all electronic states, of both odd and even molecules. According to the writer's conclusions,[4,6] j has integral values for odd molecules but half-integral values for even molecules.[18]

Electronic bands of type (*b*). The summation rule method of Fowler and Dieke leads to the conclusion that Eq. (1) should hold for electronic bands of type (*b*) as well as for bands of type (*a*). The intensity data of Frerichs[20] on the CuH bands, which are of type (*b*), show that Eq. (1) is indeed applicable here, even to the extent of accounting for the observed superior intensity of the P branch (in emission bands $E_0=E'$ and the exponential factor in Eq. (1) favors the P branch, while in absorption bands $E_0=E''$ and this factor favors the R branch[3,11,13]). The intensity relations in the analogous AgH and AuH bands appear to be of the same type. In the I_2 absorption bands, as Fowler has pointed out,[11] the approximately equal intensity of the two components

[17] The assumption made by Kemble, Fowler, and Dieke, that a ρ may be present (other than a "secondary" ρ as discussed in ref. 7, p. 1206), is then probably unnecessary if not unjustified for bands of types (*a*) and (*b*).

[18] The new quantum mechanics[14,15,16,27] formulates the rotational energy in terms of a different set of j values than those used here. For the case $j_e=0$, the result is $F(j)=B(j+\frac{1}{2})^2+\cdots$, with $j=0$, 1, 2, · · · , hence $p=2j+1$. Thus it is evident that the j values of the quantum mechanics are analogous to Sommerfeld j values (since $p=2j+1$), while the writer's j values (for which $p=2j$) are analogous to Lande J values. Since the writer has concluded[4,6] that the correct j_e values for molecules are of the Sommerfeld type, it would then be logical to adopt the j values of the quantum mechanics. Largely in order to avoid confusion of notation as compared with earlier papers, the writer's j values will, however, be used here.

[20] R. Frerichs, Zeits. f. Physik **20**, 170 (1923).

in each doublet (one P, one R line) in the "resonance spectrum," again shows the applicability of Eq. (1).

The necessary applicability of Eq. (1) to all bands of type (b) is not obvious from the correspondence principle (cf. the discussion in a preceding paragraph); such a definite result would seem to imply a particular molecular model. The solution of this difficulty probably is that precisely the model corresponding to Eq. (1) is required by nature. This idea is supported by the fact that all known bands of type (b) appear to be in agreement with Eq. (1). Again, although it is not obvious that restrictions as to model (except that $\sigma=0$ and the absence of a Q branch are assumed) are required in deriving Eq. (1) by the summation rule method, it should be noted that Eq. (1) can be obtained as a special case of a more general Eq. (4) given below which involves definite assumptions in respect to a model. From the evidence presented below in regard to bands where $\sigma\neq 0$, it is altogether probable that the model on which Eq. (4) is based is the correct one for all known bands obeying Eq. (1).

Intensity Relations in Bands Involving Rotational Terms of the Form $B(j^2-\sigma^2)$: Application of the Correspondence Principle

Application of older form of correspondence principle. In order to apply the correspondence principle to the intensity relations in bands of the type here under consideration, it is necessary to know or to assume something about the nature of the quantity σ (for the cases here considered, $\rho=0$). It will be shown below that predicted and observed intensity relations for a number of band spectra are in agreement if we assume that σ is an *electronic quantum number* which is correlated with a *precession about the internuclear axis*. This assumption is also strongly supported by the fact that in observed bands, according to interpretations recently given by the writer,[6,7] the selection rule $\Delta\sigma=0$ or ± 1 is observed.[21] Furthermore, as Hund has recently shown,[22] precisely such a precession and such a selection rule are to be expected from theoretical considerations. The relation of the results of the present and previous papers of this series to Hund's theory will be discussed in a separate paper.[23]

[21] Thus in $^1S\rightarrow{}^1S$ transitions (CuH bands etc.[6]), $\Delta\sigma=0$, while the CO Angstrom, AlH, and He_2 bands furnish examples of $\Delta\sigma=+1$ and $\Delta\sigma=-1$.

[22] F. Hund, Zeits. f. Physik **36**, 657 (1926).

[23] Strictly it is *not* σ itself, but the component σ_k of σ due to orbital electronic angular momentum, with which the precession here under discussion is correlated; σ itself is a resultant of σ_k and σ_s, where σ_s is the component along the internuclear axis of the resultant angular momentum s of electron spin; generally $\Delta\sigma_s=0$ so that $\Delta\sigma_k=\Delta\sigma$. In bands of the ZnH type ($^2P_1\rightarrow{}^2S$, $^2P_2\rightarrow{}^2S$), however, $\Delta\sigma=\frac{1}{2}$ and $1\frac{1}{2}$, but $\Delta\sigma_k=1$, indicating that σ_k is more fundamental than σ, as also follows from Hund's theory. These points will be further discussed in a later paper.

For a precession of the type indicated, the predictions of the correspondence principle for the intensitities of P, Q, and R branch lines are completely analogous to those for the transitions $\Delta j=+1$, 0, and -1 in a line spectrum multiplet. For any selected initial rotational state, if θ represents the angle between j and the figure axis (direction of σ), the intensities should then be given to a fair degree of approximation by the following proportions:[24]

$$\begin{aligned}&(a)\quad \sigma'-\sigma''=\pm 1,\ i_P : i_Q : i_R=\tfrac{1}{2}(1\mp\cos\theta)^2 : \sin^2\theta : \tfrac{1}{2}(1\pm\cos\theta)^2\\ &(b)\quad \sigma'-\sigma''=0,\ i_P : i_Q : i_R=\tfrac{1}{2}\sin^2\theta : \cos^2\theta : \tfrac{1}{2}\sin^2\theta\end{aligned}\qquad (3)$$

In the necessary averaging of the intensity factors of Eq. (3) over the initial and final states, a linear average may be expected to give good results, as in the line spectrum case. Thus suppose $\sigma'=1$, $\sigma''=0$, $j'=2\tfrac{1}{2}$. Noting that $\cos\theta=\sigma/j$, one has $\sigma'/j'=1/2\tfrac{1}{2}$, $\sigma''/j''=0$, and $i_P : i_Q : i_R=\tfrac{1}{2}[(1-1/2\tfrac{1}{2})^2+1] : [1-(1/2\tfrac{1}{2})^2+1] : \tfrac{1}{2}[(1+1/2\tfrac{1}{2})^2+1]$ $=0.68 : 1.84 : 1.48$.

Nature of ^1S states and relation to $^1S\rightarrow{}^1S$ bands. For the special case $\sigma'=\sigma''=0$, according to Eq. (3*b*), we have $\cos\theta=0$ for all values of j, and $i_Q=0$, $i_P=i_R$. This is in essential agreement with Eqs. (1) and (2).

The applicability of Eq. (2) to all known electronic bands corresponding to $^1S\rightarrow{}^1S$ transitions therefore no longer presents a difficulty but indicates that ^1S molecular states belong to the class of σ-type states, σ being correlated with a precession about the internuclear axis. The fact that ^1S molecular states combine spectroscopically with ^1P states ($\sigma=1$) supports this conclusion, which is furthermore in line with recent theoretical considerations of Hund.[22]

Hönl and London's application of the summation rule. As shown by Hönl and London,[12] Eqs. (3*a*) and (3*b*) can be replaced by more exact equations (Eqs. 4-5-6 below) obtained by an application of the summation rule. Hönl and London's treatment depends on the existance of a close formal analogy between the transitions $\Delta j=0$, ± 1 in line spectrum multiplets and the transitions $\Delta j=0$, ± 1 (Q, R, P, branches) in band spectra, and between $\Delta k=0$, ± 1 in line spectra and $\Delta\sigma=0,\pm 1$ in band spectra, and thus implicitly involves the assumption that σ is correlated with a precession about the internuclear axis as assumed above in connection with Eq. (3).

Hönl and London's equations should of course be applicable to odd as well as to even molecules, using appropriate j values in each case (Hönl and London do not consider this point at any length). The

[24] These equations are stated by Hönl and London.[12] The transitions $\Delta\sigma$ (or $\Delta\sigma_k$) $=\pm 1$ or 0 correspond to $\Delta k=\pm 1$ or 0 in the line spectrum case.

equations involve the assumption $p=2j$, which may be expected to hold equally well for odd and even molecules.[25,26]

Eq. (4) is applicable to vibration-rotation as well as to electronic bands; Eq. (2) is now seen to be merely the special case of Eq. (4) corresponding to $\sigma'=\sigma''=0$. Eqs. (5) and (6) are obviously applicable only to electronic bands.

In all cases the relation $I=ie^{-E_0/kT}$ of Eqs. (1) and (2) is applicable, but of course implies thermal equilibrium.

In Eqs. (4)-(6) as given below, Hönl and London's original equations have been considerably altered in form for the sake of convenience in application. In terms of the notation and assignment of j values here adopted, and expressed in terms of $\bar{j}$ (i. e., the mean of j' and j'') rather than of j' or j'' (for Q branches $j'=j''=\bar{j}=j$), the equations are as follows:

For the case $\sigma'=\sigma''=\sigma$,

$$\left.\begin{aligned} i_P &= i_R = 2a(\bar{j}^2-\sigma^2)/\bar{j} \\ i_Q &= 4aj\sigma^2/(\bar{j}^2-\tfrac{1}{4}) \end{aligned}\right\} \tag{4}$$

For the case $\sigma'-\sigma''=+1$,

$$\left.\begin{aligned} i_P &= a(\bar{j}-\sigma')(\bar{j}-\sigma'+1)/\bar{j} \\ i_Q &= 2aj(j-\tfrac{1}{2}+\sigma')(j+\tfrac{1}{2}-\sigma')/(\bar{j}^2-\tfrac{1}{4}) \\ i_R &= a(\bar{j}+\sigma')(\bar{j}+\sigma'-1)/\bar{j} \end{aligned}\right\} \tag{5}$$

For the case $\sigma'-\sigma''=-1$,

$$\left.\begin{aligned} i_P &= a(\bar{j}+\sigma'')(\bar{j}+\sigma''-1)/\bar{j} \\ i_Q &= 2aj(j-\tfrac{1}{2}+\sigma'')(j+\tfrac{1}{2}-\sigma'')/(\bar{j}^2-\tfrac{1}{4}) \\ i_R &= a(\bar{j}-\sigma'')(\bar{j}-\sigma''+1)/\bar{j} \end{aligned}\right\} \tag{6}$$

By applying the methods of the matrix mechanics to the closely allied case of the symmetrical rotator, Dennison[27] has obtained equations which are in complete agreement with those of Hönl and London, and there seems no reason to doubt that Eqs. (4)-(6) will remain valid, on the basis of the new quantum mechanics, for the diatomic molecule with $j_s=\sigma$.

[25] Hönl and London assume $p=2j+1$ (so that their j values are the same as those of the new quantum mechanics[18]), using, however, the designation m instead of j; they also use m_0 where σ is here used. In the present notation and j numbering, Hönl and London's m would then be replaced by $j-\frac{1}{2}$. However, m as used by Hönl and London is neither m' nor m'' specifically, but represents whichever is the larger of the two ($m=m''=\overline{m}+\frac{1}{2}$ for P, $m=m'=m''=\overline{m}$ for Q, and $m=m'=\overline{m}+\frac{1}{2}$ for R branches). It will then be readily seen that the substitution $m=j$ is correct for both P and R branches, while for Q branches $m=j-\frac{1}{2}$, if the j values are to be those here adopted.

[26] In the analogous atomic case, the relation $p=2j+1$ holds for both even and odd molecules, the j values (Sommerfeld) being integral in the former and half-integral in the latter case.

[27] D. M. Dennison, Phys. Rev. **28**, 329 (1926): Eq. (25). Dennison's m and n correspond to $j_0-\frac{1}{2}$ and σ_0 in the present notation. To get from Dennison's equations to Eqs. (4)–(6), the former must be multiplied by the factor $2j_0$, and also by certain constant factors 1, 2 or 4 (because Dennison's equations are amplitude equations).

Comparison of results of old correspondence principle with those obtained by summation rule method.[11] Since the summation rule method is supposed to involve nothing more than a refinement of the old correspondence principle, Eqs. (3) and (4)-(6) should be in asymptotic agreement for large quantum numbers. That this is the case can readily be verified. The agreement is in fact close even for small quantum numbers if we amplify and somewhat modify Eq. (3) by assuming $i = a\bar{p} = 2aj$ as in Eqs. (1) and (2), giving to a values proportional to the appropriate trigonometric functions of Eq. (3); Eq. (1) is then in agreement with Eq. (3*b*) for the special case $\sigma = 0$. Considering again the case $\sigma' = 1$, $\sigma'' = 0, j' = 2\frac{1}{2}$ as an example (cf. above, following Eq.3) one now finds $i_P : i_Q : i_R = 2.04 : 4.60 : 2.96$, whereas Eq. (5) yields the ratio 2 : 5 : 3.

Inaccuracy of Hönl and London equations for large j values. As shown by Kemble,[2] the factor a in Eq. (1) is not quite the same for the P and R branches in oscillation-rotation bands, and differs more and more as j increases. This difference is due to the variation in the moment of inertia as a result of the vibration of the molecule. The latter renders the rotation non-uniform, and affects the Fourier amplitudes which according to the correspondence principle govern the relative intensities of the P and R branches. This factor always tends to make the P branch more intense, thus assisting the Boltzmann factor in emission bands and opposing it in absorption bands. The effect of this factor remains present on the basis of the summation rule,[28] and in the new quantum mechanics.[16]

The existence of a similar effect in electronic bands seems likely, but the theory has not yet been developed. Other deviations from the relations predicted by Eq. (4)-(6) are to be expected in case of appreciable departure of the electronic angular momentum or its components from rigid orientation with respect to the internuclear axis. The experimental evidence bearing on the above points will be discussed below.

Form of theoretical intensity distribution for specific cases. Effect of Boltzmann factor. According to the preceding discussion, the relative intensities of the lines of a band are determined by the product of a factor i which represents a transition probability *times* an a priori probability $2j_0$, and a factor $e^{-E_0/kT}$, the Boltzmann factor. The factors $2j_0e^{-E_0/kT}$ assume thermal equilibrium for the initial states. This is to be expected in absorption bands, but not in emission bands as ordinarily excited. Nevertheless in practice the rotational energy distribution appears to be normally of a type corresponding well to thermal equilibrium at some specifiable "effective temperature"[29] which

[28] R. H. Fowler, Phil. Mag. **50**, 1079 (1925).

[29] The *vibrational* energy distribution does not in general take a form corresponding to thermal equilibrium (cf. R. S. Mulliken, Phys. Rev. **26**, 21–2 and 333 (1925)).

apparently approximates the actual temperature of the surroundings. The question has been examined especially by Birge,[30] in a quantitative study of intensity distribution in the violet cyanogen bands as emitted by various sources.

The types of intensity distribution to be expected for the cases $\Delta\sigma = \pm 1$ are best appreciated by an examination of the theoretical curves in Figs. 1-3 below. For these cases the Q branch is roughly twice as strong as the P or the R branch, while the two latter are roughly equal in intensity. These relations are asymptotically true for large quantum numbers, except for the effect of molecular vibration, and of the Boltzmann factor favoring the P branch. For small values of j, the relative intensities of the branches, especially of the P and R branches, depend markedly on the sign of $\Delta\sigma$ and the magnitude of σ.

It is of interest to note that, as between the P and R branches, the branch which has the larger number of missing lines[6] is always the weaker after it begins. Thus for $\sigma' = 1$, $\sigma'' = 0$, the first P line has $(j' \to j'') = (1\frac{1}{2} \to 2\frac{1}{2})$, or $\bar{j} = 2$, while the first R line has $(j' \to j'') = (1\frac{1}{2} \to \frac{1}{2})$, or $\bar{j} = 1$; for the P branch the i factors of Eq. (5) have the values 1, 2, 3, . . for $\bar{j} = 2, 3, 4, \ldots$, while for the R branch they are 2, 3, 4, . . . for $\bar{j} = 1, 2, 3, \ldots$ But for $\sigma' = 0$, $\sigma'' = 1$, the first P line has $\bar{j} = 1$ and the first R line $\bar{j} = 2$, and correspondingly the i factors for the two branches are interchanged (cf. Eq. 6) as compared with the previous case. For the case $\Delta\sigma = 0$, where the number of missing lines is the same in the P as in the R branch, the i values likewise are equal for any given value of $\bar{j}$.

The case $\Delta\sigma = 0$ (Eqs. 1 and 4) is illustrated in the present paper only for $\sigma = 0$, where the Q branch vanishes. If $\sigma > 0$, a weak Q branch is to be expected, proportional to σ^2 in intensity (cf. Eq. 4); but in all cases the intensity should fall from the beginning, asymptotically approaching zero, for large j values, as compared with those of the P and R branches.

Relation of Rotational Doubling and Alternating Intensities to the Theory

Rotational doubling. In the development of Eqs. (3)-(6) it was assumed, partly explicitly, partly implicitly, that to each value of j there corresponds just one rotational state, and that P, Q, and R branches all involve the same sets of rotational states. But in practice, as shown in a previous paper,[7] the rotational states are double (A and B sub-states) when $\sigma > 0$, and what is worse, the P and R branches involve $A \to A$ and $B \to B$ combinations, while the Q branches involve $A \to B$ and $B \to A$ combinations (cf. Fig. 1 and Eqs. 2 and 3 of ref. 7). Hence between Q branches on the one hand and P and R

[30] R. T. Birge, Astrophys. J. **55**, 273 (1922).

branches on the other there is an independence which is neither anticipated nor explained by the correspondence principle as applied in the theory outlined above. For example, in a $^1P \rightarrow {}^1S$ electronic transition ($\sigma' = 1$, $\sigma'' = 0$), there is a Q branch involving exclusively initial rotational states of the A type, and a P and an R branch each involving exclusively B-type initial states; the final rotational states are of a single type, probably[7] the B type. Similar anomalies occur in the case of $^1S \rightarrow {}^1P$, $^1D \rightarrow {}^1P$ and other transitions[7] and doubtless in general for combinations of σ-type terms.

If, however, we deliberately overlook these phenomena, by lumping together in all cases the A and B states corresponding to any particular value of j, it is possible to make a comparison between experimental intensity data and the theory as given above. The procedure is justified by the results, as will be shown below, so that it seems permissible to regard the simple theory as an essentially correct first approximation to reality. The success of this method obviously implies an equality of the a factors of Eqs. (5), (6), or (7), for Q as compared with P and R branches, and so indicates equal a priori probabilities for rotational states of the A and B types.

Alternating intensities. Another phenomenon which is not capable of being accounted for by the simple theory is that of alternating intensities in band lines. In this connection reference should be made to a previous paper[7] and to references given there. Formally, alternating intensities of the observed type can be reproduced, so far as is known from the data now available, if in Eqs. (4)-(6),—or other corresponding equations for rotational terms not of the σ type,— the factor a is permitted to have a value or set of values which differ in a constant ratio for alternate lines.[31] The same ratio is applicable to P, Q and R branches, but in such a way that all lines having a common value of j' or j'', rather than of j, are weakened or intensified. The alternation must therefore be a property of the *molecular states* involved, not of the transition probabilities. This is shown especially by the He_2 bands[7] and the N_2^+ bands.

If, as in the He_2 bands, alternate lines are completely missing in each branch, the intensities of the remaining lines can be plotted against j on a single curve which should be of the same form as if every line were present, if the above-suggested assumption of a constant ratio factor (here zero) is correct. On this basis, as will be shown below, the theoretical and observed intensity curves are in fact in agreement.

As shown in a previous paper,[7] the system of alternate missing levels in the He_2 molecule is such as to render impossible $^1S \rightarrow {}^1S$ and $^1P \rightarrow {}^1P$ transitions. This is a rather extreme example of the difficulties which

[31] Cf. also fuller discussion by J. H. Van Vleck, Phys. Rev. **28**, 980 (1926).

the phenomenon of alternating intensities presents, from the correspondence principle standpoint.

Comparison of Theory With Experimental Evidence: Bands Involving Singlet Electronic States

Singlet electronic states (^1S, ^1P, ^1D, . . . , with $\sigma = 0, 1, 2, \ldots$) are characteristic of even molecules. For these molecules the j values are half-integral.

Nature of available data. Comparatively little work has been done on the quantitative measurement of the intensities of band lines. Nevertheless there is a considerable mass of useful data, for the most part of two types (1) eye estimates of photographic blackening (2) measurements or curves of photographic density against wave-length. In the absence of disturbing factors (serious variations of plate sensitivity, etc. with wave-length; effects of impurities; unresolved doublets; lack of care to use a uniform scale in the case of eye estimates; etc., etc.), both these types of data, especially the second, are valuable in giving correctly the *order of intensity* of the lines in a band.

The value of such imformation can be seen from the following considerations. Suppose all the lines of a band (including lines on both the ascending and descending parts of the intensity curves) are arranged in order of intensity (*a*) according to theory (*b*) according to experimental data of the type mentioned. A little consideration will show that substantial agreement of the two modes of arrangement would constitute a verification of the theory falling not far short of being completely satisfactory, a chance agreement being exceedingly improbable.

With data of the type mentioned, the theoretical curves of absolute intensities and the experimental curves should usually differ mainly in the existence of a relative flattening of the latter for higher intensities: thus equalities and inequalities, but not intensity ratios, should be correctly reproduced.

Intensities in $^1S \rightarrow {}^1S$ transitions ($\sigma' = \sigma'' = 0$). The applicability of Eqs. (1) and (2) to bands involving $^1S \rightarrow {}^1S$ transitions has been discussed in the first section. Certain minor points remain to be considered. Although in the case of the HCl bands at 3.46μ the work of Kemble and Bourgin confirms the predicted greater intensity of the R branch in absorption, due to the Boltzmann factor, there are other infra-red absorption bands, as pointed out by Fowler,[11] in which the P branch appears to be the stronger. Aside from the possibility of experimental error, this may be ascribed (as Oppenheimer has intimated[16]) to a variation of the a factor of Eqs. (1) and (2) due to molecular vibration (cf. above, p. 398), in such a way as to favor the P branch, even to the extent of making it stronger than the R branch by overcoming the contrary effect of the Boltzmann factor.

The excess intensity of the P over the R branch in the CuH bands is considerably greater[11] than that predicted by the theory because of the effect of the Boltzmann factor alone. On the latter basis, the strongest P line should be about 7.5% more intense than the strongest R line, while according to Frerich's data,[20] the excess is about 27%, 13%, or 11%, in three different bands. It seems possible that the discrepancy is due to the effect of molecular vibration. Such an effect is especially likely here on account of the high temperature (about 3400°C, assuming Eq. 1),[32] which causes the maximum intensity in each branch to lie at relatively high values of j.

Intensities in $^1P \rightarrow {}^1S$ *transitions* ($\sigma' = 1, \sigma'' = 0$) *in helium bands.* The class of bands under discussion is represented, according to recent conclusions of the writer,[7,33] by a large number of helium bands, the

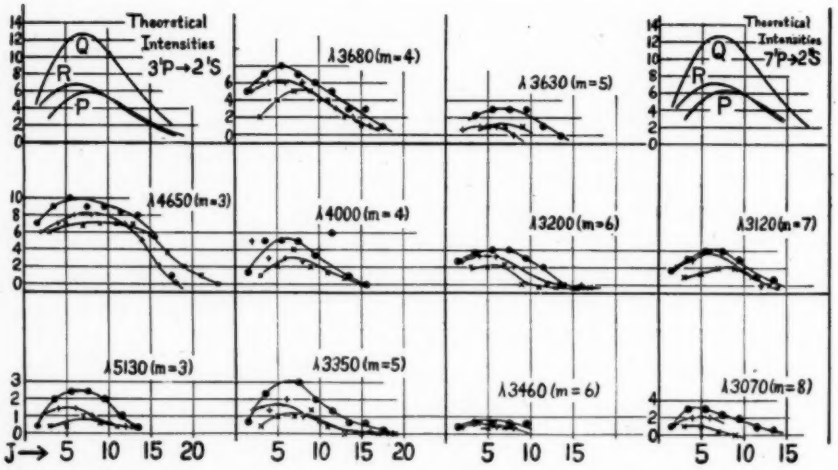

Fig. 1. Theoretical and observed intensities in $m\ ^1P \rightarrow 2\ ^1S$ helium bands of the "main" and "second" series. The theoretical intensities correspond to an assumed temperature of 700°C. The observed intensities for P, Q, and R branches, respectively, are denoted by $\times$, $\oplus$, and $+$.

"series" bands of Fowler and Curtis and Long. Although only eye estimates of intensity are available, these exist for so many bands that a good comparison with theory is possible. Such a comparison is made in Fig. 1. Theoretical curves (the intensities are of course on an arbitrary scale) are given in Fig. 1 only for two extreme cases $3^1P \rightarrow 2^1S$ and $7^1P \rightarrow 2^1S$: these and other (intermediate) cases differ, —but only slightly,—in respect to the value of E_0 as a function of j, in the Boltz-

[32] The distribution seems to be of the thermal equilibrium type. The assumption $T = 3640°K$ gives $j = 14+$ for the strongest P line and $j = 14-$ for the strongest R line, in agreement with observation.

[33] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 158 (1926).

mann factor. The temperature of 700°C assumed for all cases gives good agreement with the experimental intensity curves.[34]

The theoretical curves in Fig. 1 for the transition $3^1P \rightarrow 2^1S$ are based on the calculations given in Table I. Entirely analogous cal-

TABLE I

Calculation of theoretical intensities for helium band λ4650($3^1P \rightarrow 2^1S$ *transition*), *assuming* $t = 700°C$ ($kT = 679$). The *absolute* values of i and I are without significance here; the $I_{obs.}$ values, being eye estimates, are furthermore not directly proportional to true intensities. The values of E' and kT are in wave-number units.

P and *R* Branches

$j'-\frac{1}{2}$	E'	$e^{E'/kT}$	Designation*	i	$I_{calc.}$	$I_{obs.}$ λ4650	$I_{obs.}$ λ5130	Designation*	i	$I_{calc.}$	$I_{obs.}$ λ4650	$I_{obs.}$ λ5130
2	37	1.06	$R'(1)$	3	2.82	6	1	$P(2)$	2	1.90	6	0
4	136	1.22	2	5	4.08	7	1+	3	4	3.27	7	0
6	292	1.54	3	7	4.55	8	1+	4	6	3.90	7−	1
8	503	2.10	4	9	4.30	8	1	5	8	3.83	7	1−
10	770	3.11	5	11	3.54	8	1−	6	10	3.22	7	0
12	1090	5.00	6	13	2.60	7	0	7	12	2.40	7	0
14	1464	8.65	7	15	1.73	5	–	8	14	1.62	6−	–
16	1889	16.1	8	17	1.06	2	–	9	16	0.99	4−	–
18	2365	33	9	19	0.58	1−	–	10	18	0.55	2	–
20											1	
22											0	

* In the notation of Curtis and Long.

Q Branch

Designation	$j'-\frac{1}{2}$	E'	$e^{E'/kT}$	i	$I_{calc.}$	$I_{obs.}$ λ4650	$I_{obs.}$ λ5130
$Q(1)$	1	9	1.01	3	2.96	7	0
2	3	80	1.12	7	6.23	9	2
3	5	208	1.36	11	8.12	10	2+
4	7	391	1.78	15	8.43	9	2+
5	9	631	2.54	19	7.49	9	2
6	11	932	3.94	23	5.84	8+	1
7	13	1272	6.5	27	4.15	8	0
8	15	1677	11.8	31	2.60	6	–
9	17	2141	23.5	35	1.49	1	–

culations apply for $7^1P \rightarrow 2^1S$ and other transitions. The theoretical intensities ($I_{calc.}$) are calculated by means of the equation $I = ie^{-E'/kT}$ (for emission bands E_0 of Eq. 1 is E'). The E' values (in wave-number units) are from Curtis and Long's analysis of the λ4650 ("main series") band.[35] The E' values are nearly the same for the "second series"

[34] The intensity estimates on the bands corresponding to the most excited electronic states were made on a different set of exposures than for the remaining bands and the $^1D \rightarrow {}^1P$ and $^1S \rightarrow {}^1P$ bands discussed below, so that a different value of T might have been anticipated; the change seems, however, to be within the errors of the data.

[35] The E' values are essentially those given in Table VII of Curtis and Long's paper (Proc. Roy. Soc. **108A**, 513, 1925), except for an additive constant $-B\sigma^2$ (since $\sigma = 1$, $-B\sigma^2 = -B = -7$), due to the assumption here of the form $B(j^2-\sigma^2)$ in place of Bj^2 used by Curtis and Long.

bands as for the corresponding "main series", so that practically the same theoretical curves are applicable to both. The i values are as given by Eq. (5). The theoretical curves are obtained by plotting the calculated I values against j. Of course we are really dealing with a discontinuous function, so that the continuous curves are of significance only as an aid to the eye in appreciating the relation of the points through which they are drawn. Furthermore, in drawing the curves (both theoretical and experimental) the points corresponding to alternate j values (which strictly should be plotted with zero intensity) have been disregarded. This matter has been discussed in a previous section (p. 400).

A comparison of the theoretical and experimental curves on the above basis, bearing in mind the various possible causes of distortion and error in the experimental curves, indicates that the two are in essential agreement. Considering individual bands, the agreement is not always very good, but the deviations seem irregular, and most of them disappear if one replaces the individual curves in imagination by an average curve. Individual deviations may be only apparent and due to the crudeness of the method of recording intensities, or they may in some cases be due to perturbations (also, see below).

The agreement with theory may be described under the following headings:

(1) The Q branch is always the strongest, and, so far as can be seen from the data, may well actually be twice as strong as either of the other two branches, as predicted; the latter relation is indicated especially in the bands of low intensity, where the estimates of blackening are more nearly proportional to true intensity.

(2) The values of j for the *strongest line* in each branch are on the whole in the correct order $P>Q>R$, and differ by the correct amounts; these j_{max} values are moreover practically the same in all the bands, showing that the same effective temperature applies to all.

(3) The R branch is always markedly stronger than the P branch for small j values (the first R line is approximately twice as strong as the first P line, although j is only two thirds as great), while for large j values the two branches are asymptotically about equal in intensity. The first R line is about equal in intensity to the first Q line.

In spite of the crudity of the intensity data, the experimental curves are thus unmistakably of the predicted type for $\sigma'=1$, $\sigma''=0$, and equally unmistakably are different from the predicted types for any other pair of values of σ' and σ'', even for the same value of $\Delta\sigma$ (cf. curve for $\sigma'=2$, $\sigma''=1$, in Fig. 2). The agreement is all the more remarkable in view of the fact that alternate lines in each branch are missing, and in view of the existence of rotational doubling, since neither of these facts is anticipated by the theory. It is important

to note that the agreement would not exist if the j values had not been assigned on the assumption of alternate missing lines.

Taken together with the evidence previously given,[7] the present results seem to constitute conclusive evidence in favor of the interpretation of the He_2 bands given in previous papers.[33,7]

The fact that the agreement with theory is not disturbed by the circumstance that the Q lines arise from A rotational sub-states and the P and R lines from B sub-states indicates (among other things) that the two sub-states have equal a priori probabilities (cf. discussion above, p. 399)

There seem nevertheless to be certain systematic minor deviations from the theoretical curves. For the bands involving highly excited initial electronic states, there is a tendency toward more rapid decrease of intensity for high j values than the theory calls for. For the most excited states, there even seems to be a shift, for the line of maximum intensity in each branch, toward a lower value of j than predicted. These effects can probably be attributed to a marked instability of molecules having high j values, especially for the higher electronic states (such instability is also indicated by the setting in of a rapid diminution in the rate of growth of the spacing of the rotational energy levels). Due to this instability, such molecules are presumably reduced in numbers below the proportions corresponding to statistical equilibrium. The question of instability has been discussed by Curtis.[36]

Other $^1P \rightarrow {}^1S$ *transitions: the* AlH *Bands.* Primarily on the basis of missing lines, the known AlH band system has been classified[7] as corresponding to a $^1P \rightarrow {}^1S$ electron transition. The bands should therefore show intensity relations similar to those in the He_2 bands just discussed, but without the complication of alternate missing lines. According to Eriksson and Hulthén,[37] the Q branch is approximately twice as strong as the P or R branch, as it should be for a $^1P \rightarrow {}^1S$ (or $^1S \rightarrow {}^1P$) transition. The intensities (eye estimates) given by Eriksson and Hulthén give indications of the expected superior intensity of the R as compared with the P branch for low j values; the same is true of the data of Mörikofer[38] on the same bands (for "Form I" of the discharge).

A more definite confirmation of the predicted intensity relations is obtained by a study of a photometer curve of the $\lambda 4354$ ($n' \rightarrow n'' = 1 \rightarrow 1$) band as given by Eriksson and Hulthén. So far as can be seen, the intensities are in agreement with prediction (for thermal equilibrium at a fairly high temperature), but it does not seem worth while to make a detailed comparison, since there is much superposition of lines

[36] W. E. Curtis, Proc. Roy. Soc. **103A**, 315 (1923).

[37] G. Eriksson and E. Hulthén, Zeits. f. Physik **34**, 775 (1925). In regard to the intensity of the Q branch, cf. footnote on p. 777.

[38] W. Mörikofer, Dissertation Basel, 1925.

from different branches. The peaks corresponding to the first line of the R branch ($j=1$) and the second line of the P branch ($j=3$) are, however, fairly free from neighboring peaks,[39] and their intensities are seen to be roughly equal, in agreement with the theoretical prediction that $i=2$ for both (cf. Eq. 5). This, in connection with the evident superiority of intensity of the Q branch, is good evidence that the intensity relations are of the predicted type. The observed relations may be contrasted with those predicted for the case $\sigma'=\sigma''=0$, where the intensities of the lines mentioned should be in the ratio 1 : 3, and with those for $\sigma'=0$, $\sigma''=-1$, where the R line in question should be *absent*, and the P line should have $i=4$.

Intensity relations in $^1D\rightarrow{}^1P$ *transitions* ($\sigma'=2$, $\sigma''=1$): *the helium band* λ 5733. In previous papers[7,33] it was concluded that He_2 λ5733 is the (only known) representative of a $^1D\rightarrow{}^1P$ transition, with $\sigma'=2$, $\sigma''=1$. The intensity data in Table II below are eye estimates by Curtis.[40] The corresponding theoretical intensities are obtained in much the same way as for the $^1P\rightarrow{}^1S$ transitions in He_2, using the relation $I=ie^{-E'/kT}$, calculating the i values from Eq. (5), and assuming the same effective temperature (700°C) as in the previous case, since the photographs were made under the same conditions. In one respect the procedure is different, due to the fact that the λ5733 band has six branches (two of each type), as compared with three for the bands previously discussed; this is due to the occurrence of rotational doubling for both ^1D and ^1P states.[7] As in the $^1P\rightarrow{}^1S$ bands, each branch has alternate lines completely missing. This, however, occurs in such a way that one P, one Q and one R line is present for each value of j' or j'' (above $j'_{\text{min.}}$ or $j''_{\text{min.}}$), and in Fig. 2 all these lines have been plotted in a continuous series for the experimental as well as for the theoretical curves. The theoretical intensities of course lie (nearly) on a continuous curve, since the theory makes no provision for rotational doubling, except in so far as this affects the value of $E'(j)$[41]. The fact that the observed intensities also lie on smooth curves in spite of the fact that the intensities for alternate values of j correspond to different rotational sub-states, indicates that (as in the "series" bands) the two sub-states (A and B) are alike in respect to their a priori probabilities, etc. If the present discussion does not make these points clear, a study of Fig. 2 and Table II, in connection with the discussion of He_2 λ5733 in ref. 7, should do so.

From Fig. 2 and Table II it is evident that the substitution of $\sigma'=2$ for $\sigma'=1$, without any change in $\Delta\sigma$, is enough to produce a very great

[39] In the notation of Eriksson and Hulthén, these lines are $R(1)$ and $P(4)$.

[40] W. E. Curtis, Proc. Roy. Soc. **101A**, 38 (1922).

[41] As a matter of fact, the values of E' (j) fall into two sets which are sufficiently different so that the theoretical curve should not be quite smooth (cf. Table II); for convenience, however, a smooth curve has been drawn in Fig. 2.

TABLE II

Calculation of theoretical intensities for helium band λ5733 ($3^1D \rightarrow 2^1P$ *transition*) *assuming* $t = 700°C$

See note at top of Table I. The "Designations" are those given by Curtis,[40] and also used by Kratzer. For the experimental I data, see Fig. 2 or ref. 40. The E' values for $j' = 2\frac{1}{2}, 4\frac{1}{2}, 6\frac{1}{2}, \cdots$ are $F'_A(j)$ values. These values were obtained as follows: (*a*) $E'(2\frac{1}{2})$ and $E'(3\frac{1}{2})$ were first calculated from $E \backsim B(j^2 - \sigma^2) = B(j^2 - 4)$, using $B_A = B_B = 7.56$, $\sigma = 2$, as given in ref. 7; (*b*) then making use of the $\Delta_2 F'$ values given by Kratzer (Zeits. f. Physik **16**, 353, 1923), the remaining E' values were obtained by suitable summation (by definition,—see ref. 6, Eqs. 10,—$\Delta_2 F(j) = F(j+1) - F(j-1)$). E. g., $E'_A(4\frac{1}{2}) = E'_A(2\frac{1}{2}) + \Delta_2 F'_A(3\frac{1}{2})$; $E'_A(6\frac{1}{2}) = E'_A(4\frac{1}{2}) + \Delta_2 F'_A(5\frac{1}{2})$, etc., while $E'_B(5\frac{1}{2}) = E'_B(3\frac{1}{2}) + \Delta_2 F'_B(4\frac{1}{2})$, etc. The quantities here designated $\Delta_2 F'_A(3\frac{1}{2})$, $\Delta_2 F'_A(5\frac{1}{2}), \cdots$, and $\Delta_2 F'_B(4\frac{1}{2})$, $\Delta_2 F'_B(6\frac{1}{2}), \cdots$, are respectively identical with Kratzer's $\Delta F_2(1)$, $\Delta F_2(2), \cdots$, and $\Delta F_1(2)$, $\Delta F_1(3), \cdots$ (cf. Kratzer's Table 6, p. 359). The E' values for $j' = 17\frac{1}{2}$ to $20\frac{1}{2}$ were estimated approximately by extrapolation.

$j' - \frac{1}{2}$	E'	$e^{-E'/kT}$	Designation	i	I
2	17	1.03	$R'(1)$	6	5.85
3	62	1.10	$R(2)$	6 2/3	6.09
4	122	1.19	$R'(2)$	7 1/2	6.30
5	199	1.34	$R(3)$	8 2/5	6.27
6	287	1.53	$R'(3)$	9 1/3	6.10
7	395	1.79	$R(4)$	10 2/7	5.75
8	510	2.12	$R'(4)$	11 1/4	5.31
9	650	2.60	$R(5)$	12 2/9	4.70
10	790	3.20	$R'(5)$	13 1/5	4.13
11	963	4.14	$R(6)$	14 2/11	3.43
12	1126	5.26	$R'(6)$	15 1/6	2.88
13	1332	7.10	$R(7)$	16 2/13	2.28
14	1516	9.3	$R'(7)$	17 1/7	1.84
15	1756	13.2	$R(8)$	18 2/15	1.37
16	1958	17.8	$R'(8)$	19 1/8	1.07
17	(2232)	27.1			
18	(2449)	37			
19	(2755)	60			
20	(2987)	82			

$j' - \frac{1}{2}$	Designation	i	I	Designation	i	I
2	$Q_2(1)$	3 1/3	3.25	$P(2)$	2/3	0.65
3	$Q_1(1)$	5 5/6	5.33	$P'(2)$	1 1/2	1.37
4	$Q_2(2)$	8 1/10	6.81	$P(3)$	2 2/5	2.02
5	$Q_1(2)$	10 4/15	7.66	$P'(3)$	3 1/3	2.48
6	$Q_2(3)$	12 8/21	8.09	$P(4)$	4 2/7	2.80
7	$Q_1(3)$	14 13/28	8.08	$P'(4)$	5 1/4	2.94
8	$Q_2(4)$	16 19/36	7.80	$P(5)$	6 2/9	2.94
9	$Q_1(4)$	18 26/45	7.15	$P'(5)$	7 1/5	2.77
10	$Q_2(5)$	20 34/55	6.44	$P(6)$	8 2/11	2.56
11	$Q_1(5)$	22 43/66	5.48	$P'(6)$	9 1/6	2.22
12	$Q_2(6)$	24 53/78	4.69	$P(7)$	10 2/13	1.93
13	$Q_1(6)$	26 64/91	3.76	$P'(7)$	11 1/7	1.57
14	$Q_2(7)$	28 76/105	3.09	$P(8)$	12 2/15	1.31
15	$Q_1(7)$	30 89/120	2.33	$P'(8)$	13 1/8	0.99
16	$Q_2(8)$	32 103/136	1.84	$P(9)$	14 2/17	0.79
17	$Q_1(8)$	34 118/153	1.28	$P'(9)$	15 1/9	0.56
18				$P(10)$	16 2/19	0.45
19				$P'(10)$	17 1/10	0.29
20				$P(11)$	18 2/21	0.22
				$P'(11)$		

change in the quantitative theoretical intensity relations. The *observed* intensities lie on curves which agree very closely in form (including the position of the line of maximum intensity) with the theoretical curves. The predicted very high intensity of the first few R lines and the corresponding very low intensity of the first P lines are verified. These agreements give powerful support to the interpretation of the band as having $\sigma'=2$, $\sigma''=1$.

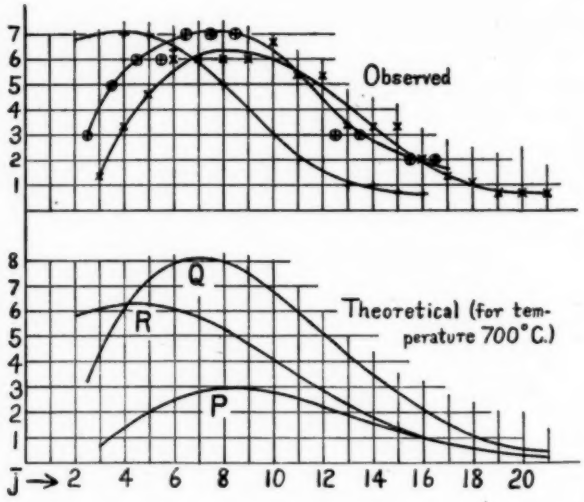

Fig. 2. Intensity relations in λ5733 helium band ($3\,{}^1D \rightarrow 2\,{}^1P$). The "observed" points are Curtis's estimates,[40] except that for the P lines Curtis's estimates have been multiplied by 2/3 (cf. text). Points where two or more lines are superposed have been omitted. Thus Q_1 (5), Q_2 (7), and R' (1) are all superposed (the calculated position of Q_2 (7) is 17467.85, in sufficiently good agreement with that of an observed line for which $\nu=17467.30$). The previously unassigned line $\nu=17471.64$ (int. 2) is evidently Q_2 (8). It is possible that Q_1 (8) is present and superposed on R' (2). It seems probable that the apparent abnormally high intensity of P' (5) is due to the superposition of a line not belonging to the band.

In certain respects the observed intensities of Fig. 2 and Table II seem to disagree with the theory: the Q branch as a whole is relatively too weak and the P branch is much too strong, in spite of the fact that in Fig. 2 Curtis's intensity estimates[38] for the P branch have been multiplied by a factor 2/3 before plotting (partial justification for this procedure is obtained by an examination of the reproduction given by Curtis, in which the P branch appears relatively considerably weaker than Curtis's data indicate). It seems possible that the apparent high intensity of the P branch may be largely due to change of plate sensitivity with wave-length (the P branch extends from λ5821 to λ5748, the Q branch from λ5733 to λ5716, the R branch from λ5724 to λ5646,

and in this part of the spectrum rapid changes of plate sensitivity occur for some types of plates; Curtis does not state what type of plate he used). It also seems possible that a different intensity scale may have been (more or less unconsciously) used for the eye estimates in the different branches. The high intensity of the P branch might also be due partly to variability in the a factor of Eq. (5). Further experimental work is needed.

Intensity relations in $^1S \rightarrow {}^1P$ *transitions* ($\sigma'=0$, $\sigma''=1$): *helium bands* λ4546 *and* λ6400. The helium bands λ4546 and λ6400 correspond to transitions $4^1S \rightarrow 2^1P$ and $3^1S \rightarrow 2^1P$ ($\sigma'=0$, $\sigma''=1$ in both cases), according to the conclusions of previous papers.[7,33] Eye estimates of intensity[40] are available. In Table III these are compared with the theoretical

TABLE III

Intensities in helium bands λ4546 *and* λ6400 ($4^1S \rightarrow 2^1P$ *and* $3^1S \rightarrow 2^1P$ *transitions*), *assuming* $t=700°C$.

See note at head of Table I. The numbers under the headings R, Q, and P, are Curtis's designations[40] for the lines of the three branches.

j′−½	E'	$e^{E'/kT}$	R	i	$I_{calc.}$	$I_{obs.}$ λ4546	λ6400
1	16	1.02					
3	88	1.14	1	2	1.76	3	(8)
5	218	1.38	2	4	2.90	3	8
7	405	1.82	3	6	3.30	3	9
9	648	2.60	4	8	3.08	3	10
11	947	4.03	5	10	2.48	3	6
13	1300	6.78	6	12	1.77	1	3
15	(1707)	12.3					

j−½	Q	i	$I_{calc.}$	$I_{obs.}$ λ4546	λ6400	P'	i	$I_{calc.}$	$I_{obs.}$ λ4546	λ6400
1	1	3	2.93	3	10	1	3	2.93	4	10
3	2	7	6.16	4	10	2	5	4.40	6	10
5	3	11	7.99	6	10	3	7	5.08	6	10
7	4	15	8.26	6	10	4	9	4.96	6	10
9	5	19	7.30	6	10	5	11	4.23	6	10
11	6	23	5.70	5	10	6	13	3.22	6	10
13	7	27	3.98	4	8	7	15	2.21	3	—
15	8	31	2.51	3	3	8	17	1.38	1	

intensities, assuming $t=700°C$ as for the other helium bands, but using Eq. (6) in calculating the i values. The predicted intensities are similar to those for $^1P \rightarrow {}^1S$ transitions except that here the P branch should be stronger than the R branch throughout its course, but especially at the beginning.

The observational data are not very satisfactory. For λ6400 the recorded intensities indicate that the plate was overexposed, no distinction being made between lines exceeding a certain intensity. However, in both λ6400 and λ4546 the predicted relatively low intensity of the

R branch is verified, and for λ4546 the data on the Q branch indicate agreement with the theory.

In both bands, as in He_2 λ5733, the recorded intensities of the P branch lines are greater, relatively to those of the Q branch, than one would expect from the theory. If these deviations are real, they might perhaps be ascribed to the effect of nuclear vibration (but $n' = n'' =$ only $\frac{1}{2}$, probably), or to a lack of rigid binding of σ(cf. above, p. 398). Further more careful intensity measurements will be needed before definite conclusions can be reached.

Even with the present data there can, however, be no doubt that the bands have an intensity distribution entirely different from those in $^1P \rightarrow {}^1S$ and $^1D \rightarrow {}^1P$ bands, and differing from these in at least qualitatively the correct way.

New data on helium bands: note added in proof. McLennan, Smith, and Lea have recently published intensity data on a number of helium bands at low temperatures (walls of discharge tube at 21°K., 85°K., and 300°K. in various runs).[42] The data on the relative intensities of the P and R branches are in excellent agreement with the theory for the ($^1P \rightarrow {}^1S$) bands λλ4650, 5130, 3680, 4000, 3630, and for the ($^1S \rightarrow {}^1P$) bands λλ4546 and 6400. In the latter case, the new data furnish a welcome supplement to those of Table III, although the absence of data on the Q branches is unfortunate. In the former case, the Q branches are more intense than the P and R branches, as expected, although apparently not twice as intense; however, it is not clear whether the data are supposed to be quantitative. The data for λ5733 ($^1D \rightarrow {}^1P$), on the P and R branches only, are in poorer agreement with the theory than are those of Curtis.—In respect to the values of j for the strongest line of each branch, a sample calculation indicates that the observed distributions correspond to the low temperatures used. But the branches fade out much too slowly with increasing j; this probably means that a considerable fraction of the molecules were in a region of relatively high effective temperature.

Intensity relations in $^1S \rightarrow {}^1P$ transitions: CO *Angstrom bands.* In a previous paper,[6] the CO band system of Ångström and Thalen has been interpreted as due to an electron transition for which $\sigma' = 0, \sigma'' = 1$. Photographs of these bands were recently taken by the writer in the second order of the 21 foot concave grating at Harvard University. The bands were excited by a transformer discharge in CO_2 at low pressure. The photographs were taken in connection with a study of the Zeeman effect and were not intended for photometric work; it was found later that the exposures without field offered valuable material for the present work.

[42] J. C. McLennan, H. G. Smith, and C. A. Lea, Proc. Roy. Soc. **113A**, 183 (1926).

In order to obtain more accurate data than would be secured by eye comparisons, a photometer curve was run on the λ4835 band ($n'=0$, $n''=1$), with the kind assistance of Dr. H. A. Barton, using the microphotometer at Princeton University. The galvanometer readings (proportional to intensity of light transmitted through the plate) for the center of each band line were then taken from the curve. Each such reading was then subtracted from the "fog" reading for a neighboring region between band lines. The results were plotted against j in Fig. 3,

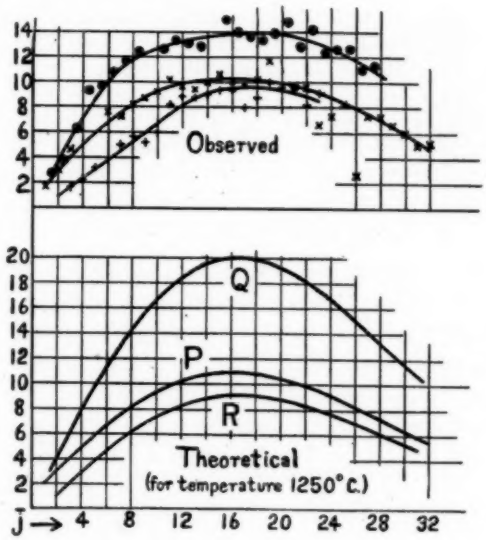

Fig. 3. Intensity relations in CO Angstrom and Thalen band ($^1S \rightarrow {}^1P$) at λ4835.

omitting, however, data on lines which were imperfectly resolved by the photometer. Results obtained in the above manner are similar in meaning to eye estimates, but more reliable.[43]

Bearing in mind the nature of the data, the agreement between the theoretical and experimental curves as shown in Fig. 3 (assuming an effective temperature of 1250°C) is very satisfactory throughout the range of j values for which data were obtained. As predicted, the P branch is stronger than the R branch throughout its course, and much stronger at the beginning, while the Q branch is stronger than either the P or the R branch. As in other cases, however, the P branch seems to be slightly stronger than is predicted with the assumption that a in Eq. (6) is constant; as already discussed on p. 398, this effect may

[43] By making assumptions as to the characteristics of the plate, semi-quantitative intensity data might have been obtained, but this did not seem worth while at the time on account of the doubtfulness of the necessary assumptions.

perhaps be attributed to vibration of the molecule.[44] The extent of the agreement between theory and experiment can best be verified from the theoretical curves by picking out various pairs or sets of lines whose intensities should be equal, and comparing with the experimental curves. Examination of other CO bands of the same system disclosed similar intensity relations, but no detailed measurements were made.

Intensity Relations in Bands Involving Doublet and Higher Electronic States

Eqs. (4)–(6) may be expected to hold in general for odd as well as for even molecules, for bands involving, in both the initial and final states, rotational terms of the form $B(j^2-\sigma^2)+\cdots$. Thus Eq. (4) should apply to ${}^2P_1\rightarrow{}^2P_1$ and ${}^2P_2\rightarrow{}^2P_2$ transitions; this is confirmed by experiment, as will be shown by Barton, Jenkins, and the writer in a later paper. Similarly in ${}^2D\rightarrow{}^2D$, ${}^3P\rightarrow{}^3P$ and other combinations, Eqs. (4)–(6) should hold.

When rotational terms of the form $B(j-\rho)^2+\cdots$ are involved in one or both electronic states, Eqs. (4)–(6) are inapplicable and it is not obvious what relations should take their place. Nevertheless, the observed intensity relations seem to be at least qualitatively in agreement with these equations. Thus for ${}^2S\rightarrow{}^2S$ transitions (violet CN band type, type (*c*) of the first section of this paper) the obvious structure and intensity relations are the same as for ${}^1S\rightarrow{}^1S$ (type *b*) transitions, except that each line is a doublet, due to the presence of a ρ with approximately the values $\pm\frac{1}{2}$. In ${}^2P_1\rightarrow{}^2S$ and ${}^2P_2\rightarrow{}^2S$ transitions ($j_e'=\sigma=\frac{1}{2}$ or $\frac{3}{2}$, $j_e''=\rho=\pm\frac{1}{2}$), the intensity distributions in the various branches in known cases (ZnH, CdH, and HgH bands) shows a resemblance to those for other transitions such as ${}^1P\rightarrow{}^1S$ where σ decreases during emission.

The writer wishes to express his appreciation of the stimulating discussion and valuable criticism of Professor E. C. Kemble.

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November 13, 1926.

[44] The anomalous intensity of the *P* line $j=26$ (perhaps also of other lines) is due to a perturbation; this line is also shifted a considerable distance from its expected position.

ROTATIONAL TERMS IN THE MgH BANDS

By William W. Watson and Philip Rudnick

Abstract

Rotational term data for the green MgH bands.—The values of the rotational terms for the vibrational states 1/2, 3/2, and 5/2 in the green MgH bands are tabulated.

Analytical representation of the terms. The Kratzer, Kramers and Pauli formula is applied to the data with the following values giving the best fit: $j'_{min}=\frac{1}{2}$, $j''_{min}=\frac{1}{2}$, $\sigma'=\frac{1}{2}$, σ'' small ($<\frac{1}{4}$), ϵ' and ϵ'' small ($\leqq 0$). The term $m=1$ exists, thereby making it impossible to let $j=m-1$. Other predicted electronic quantum numbers are shown to agree less well with the observed ΔF values.

I. Introductory

IT IS the intent of this paper to supplement an earlier description of the MgH band spectrum[1] with a more complete tabulation and discussion of the rotational term values therein involved. These and similar data should come into critical reconsideration in the general program of correlation between band and series spectra which is being carried forward by such work as that of Mulliken,[2] Mecke,[3] and in particular a recent theoretical paper by Hund.[4]

Wave-numbers for the first six branches in the band λ5211, which are assigned the vibrational quantum numbers $n'=n''=\frac{1}{2}$,[5] are given in Table I. Tables II and III give values of ΔF for initial and final electron levels (single and double primes) and for several vibrational levels. The values for the levels in which $n=\frac{1}{2}$ are most complete and will be used for further discussion. They are taken from the P and R branches alone because of the probable anomaly in the Q branches.[6] Successive differences (Δ^2F and Δ^3F) of ΔF are also tabulated for later convenience.

[1] Watson and Rudnick, Astrophys. J. **63**, 20 (1926).

[2] Mulliken, Proc. Nat. Acad. Sci. **12**, 144, 338 (1926). Phys. Rev. **28**, 481, 1202 (1926).

[3] Mecke, Zeits. f. Physik **36**, 802 (1926).

[4] Hund, Zeits. f. Physik **36**, 657 (1926).

[5] In the authors' earlier paper this band was designated as the (0, 0) band. For more recent evidence in favor of the use of half-integral vibrational quantum numbers, see Watson, Nature, **117**, 692 (1926).

[6] For an explanation of the "combination defect" introduced by the Q branch see Mulliken, Phys. Rev. **28**, 1206 (1926).

TABLE I

Wave-numbers in the MgH *band* λ5211, $n'=n''=\frac{1}{2}$

m	$P_1(m)$	$P_2(m)$	$Q_1(m)$	$Q_2(m)$	$R_1(m)$	$R_2(m)$
1			19273.39		19287.93	
2	19261.74		75.96		301.26	
3	52.91		78.28		15.19	19318.70
4	43.83		81.07		29.88	33.14
5	35.03	19239.52	84.00	19287.64	45.06	48.13
6	26.98	30.50	87.93	90.68	60.90	63.53
7	19.39	22.40	92.47	94.79	77.23	79.69
8	12.98	15.26	97.45	99.68	94.21	96.50
9	06.39	08.86	303.31	305.24	411.85	414.03
10	01.04	03.28	09.75	11.53	30.20	32.26
11	196.39	198.54	16.74	18.70	49.06	51.03
12	92.52	94.70	24.56	(26.50)	68.55	70.50
13	89.36	91.38	33.20	34.84	88.57	90.38
14	86.93	89.36	42.28	43.86	509.18	510.95
15	85.20	87.66	52.12	53.67	30.58	32.27
16	84.91	——	62.64	64.18	52.01	53.96
17	84.91	——	73.79	75.25	74.37	76.11
18	85.69	87.66	85.71	87.19	97.05	98.89
19	87.66	89.36	98.22	99.67	620.34	622.16
20	90.04	91.83	411.36	412.82	44.05	45.83
21	93.37	95.17	25.21	26.53	68.33	69.68
22	97.40	99.28	39.67	41.08	92.92	94.75
23	202.27	204.18	54.74	56.11	718.11	719.95
24	07.98	09.82	70.50	71.84	43.62	45.44
25	14.40	16.33	86.74	88.10	69.61	71.52
26	21.61	23.60	503.66	505.02	96.02	98.03
27	29.74	31.62	21.11	22.48	822.84	824.64
28	38.50	40.44	39.35	40.55	49.97	51.76
29	48.14	50.02	57.83	59.21	77.40	79.27
30	58.49	60.39	77.25	78.57	905.12	907.35
31	69.70	71.57	97.05	98.31	33.40	35.06
32	81.72	83.57	617.20	618.58	61.67	63.53
33	94.79	96.33	38.13	39.49	90.49	92.35
34	307.98	309.75	59.53	60.91	20019.33	20021.20
35			81.46	82.81	48.58	50.41
36			703.89	705.24	77.94	79.75
37			26.75	28.12	107.83	109.66
38			50.00	51.36	37.46	39.23
39			73.89	75.31	67.26	68.99
40			98.03	99.66		

II. ANALYTICAL REPRESENTATION OF THE TERMS

It is instructive to inquire in just what measure the usual Kratzer, Kramers and Pauli term

$$F(m)=B[(j^2-\sigma^2)^{1/2}-\epsilon]^2+\cdots \qquad (1)$$

will satisfactorily represent the data of Table II. For convenience, ϵ is preceded by a negative sign, and allowed negative values to accord

with Kratzer's theory of narrow doublets. m is here used merely as a counting-number arising in the empirical ordering of the bandlines; j is the rotational quantum number. From (1) with satisfactory approximation,

$$\Delta F(m) = F(m+1) - F(m-1) = 4B(j-\epsilon) - 2B\epsilon\sigma^2/(j^2-1) \quad (2)$$

Succeeding differences may then be written:

$$\Delta^2 F(m) = \Delta F(m) - \Delta F(m-1) = 4B + 4B\epsilon\sigma^2/(j^3 + \cdots) \quad (3)$$

$$\Delta^3 F(m) = \Delta^2 F(m) - \Delta^2 F(m-1) = -6B\epsilon\sigma^2/(j^4 + \cdots) \quad (4)$$

The $\Delta^3 F$'s in Table II correspond to that in (4).

TABLE II

Term values for the lowest vibrational state, $n = \frac{1}{2}$

	Initial State $\Delta F'(m) = F'(m+1) - F'(m-1)$			Final State $\Delta F''(m) = F''(m+1) - F''(m-1)$		
		Successive differences			Successive differences	
m	$\Delta F'(m)$	$\Delta^2 F'(m)$	$\Delta^3 F'(m)$	$\Delta F''(m)$	$\Delta^2 F''(m)$	$\Delta^3 F''(m)$
	a. Terms arising from the low-frequency doublet components					
2	39.30			35.02		
3	62.41	23.11		57.43	22.41	
4	86.10	.69	+.58	80.16	.73	+.32
5	110.00	.90	+.21	102.90	.74	+.01
6	133.97	.97	+.07	125.67	.77	+.03
7	57.94	.97	.00	48.32	.65	−.12
8	81.78	.84	−.13	70.84	.52	−.13
9	205.38	.60	−.24	93.45	22.61	+.09
10	29.21	.83	+.23	215.44	21.99	−.62
11	252.63	.42	−.41	237.85	22.41	+.42
12	76.14	.51	+.09	59.88	.03	−.38
13	99.24	.10	−.41	81.49	21.61	−.42
14	322.16	22.92	−.18	303.13	.64	+.03
15	44.89	.73	−.19	24.20	.07	−.57
16	367.09	.20	−.53	345.38	.18	+.11
17	89.40	.31	+.11	66.19	20.81	−.37
18	411.19	21.79	−.52	86.71	.52	−.29
19	32.67	.48	−.31	406.92	.21	−.31
20	53.98	.31	−.17	26.92	.00	−.21
21	474.96	20.98	−.33	446.58	19.66	−.34
22	95.52	.56	−.42	65.99	.41	−.25
23	515.84	.32	−.24	84.94	18.95	−.46
24	35.64	19.80	−.52	503.71	.77	−.18
25	55.21	.57	−.23	22.01	.30	−.47
	b. Terms arising from the high-frequency doublet components					
4				79.18		
5	108.61			102.64	23.46	
6	133.03	24.42		125.73	.09	−.37
7	57.29	.26	−.16	48.27	22.54	−.55
8	81.24	23.95	−.31	70.83	.56	+.02
9	205.17	.93	−.02	93.22	.39	−.17
10	28.98	.81	−.12	215.49	.27	−.12
	(These terms become identical with the above for large values of m)					

First, it may be noted that the right member of (4) vanishes for large values of m, while the corresponding experimental values are definitely finite and negative. For low values of m, Δ^3F is positive for the low-frequency doublet components and negative for the high-frequency components. The two cases may be distinguished analyti-

TABLE III

Term values for higher vibrational states taken from the low-frequency doublet components

	Initial State $\Delta F'(m)=F'(m+1)-F'(m)$		Final State $\Delta F''(m)=F''(m+1)-F''(m)$	
	For the vibrational state $n=3/2$		For the vibrational state $n=5/2$	
m	$\Delta F'(m)$	$\Delta F''(m)$	$\Delta F'(m)$	$\Delta F''(m)$
3	35.99	33.34	34.66	32.15
4	47.50	44.48	45.95	42.88
5	59.13	55.35	57.17	53.55
6	70.74	66.41	68.20	64.14
7	82.30	77.32	79.58	74.71
8	93.85	88.15	90.83	85.34
9	105.36	98.88	101.77	95.50
10	16.50	109.75	12.86	105.85
11	128.00	120.43	123.63	116.19
12	39.34	30.95	34.43	26.21
13	50.30	41.47	45.12	36.42
14	61.33	51.70	56.12	46.38
15	72.18	61.91	66.16	56.17
16	183.01	172.10	176.68	165.68
17	93.44	81.95	86.33	75.38
18	203.97	91.85	96.24	84.77
19	14.43	201.63	206.40	94.15
20	24.46	11.12		
21	234.47	220.42		
22	44.22	29.57		
23	53.99	38.68		
24	63.34	47.65		
25	72.29	55.92		

cally as having respectively negative and positive values for ϵ. This is the usual procedure, and is obviously indicated by the right member of (4). The sign of ϵ can be changed, however, only by a displacement[7] of the values assigned to j. Consequently, if the two lines in a doublet are to be associated with terms having ϵ's of opposite signs, those terms must also have different rotational quantum numbers.

Mulliken has suggested (ref. 2) that the emission of these bands is due to a transition $3^1S-3^3P_1$ in the Mg atom, that $\epsilon' \cong \epsilon'' \cong \pm\frac{1}{2}$, $\sigma' \cong 1$, and $\sigma'' \cong 0$. Now on applying Eq. (2) to the observed ΔF's of

[7] Refer to (2). The right member of the equation depends upon j and ϵ principally through the difference $(j-\epsilon)$, and accordingly, in order to give ϵ any desired value, it is only necessary to let j differ from the counting-number m by a suitable constant.

Table II, one finds that the quantity $(j-\epsilon)$ has half-integral values in both initial and final states, and consequently if the ϵ's equal $\frac{1}{2}$, both j' and j'' must have integral values. The following expressions of the form (1) with the customary fourth power term added must then represent numerically the terms of Table II for moderate values of m:

Low-frequency components:

$$F'(m) = 6.00[\{(m-1)^2-1\}^{1/2}+\tfrac{1}{2}]^2-.000336[\quad]^4 \quad (5a)$$

$$F''(m) = 5.70[\{(m-1)^2\}^{1/2}+\tfrac{1}{2}]^2-.000332[\quad]^4 \quad (5b)$$

High-frequency components:

$$F'(m) = 6.00[\{m^2-1\}^{1/2}-\tfrac{1}{2}]^2-.000336[\quad]^4 \quad (5c)$$

$$F''(m) = 5.70[m-\tfrac{1}{2}]^2-.000332[\quad]^4 \quad (5d)$$

The values of B and ϵ, except for the arbitrary constant which may be introduced, are quite definitely determined by the experimental data; merely the order of magnitude is indicated for σ^2. The coefficients of the fourth power terms were computed from the Kratzer formula[8] $\omega_0=(-4B^3/D)^{1/2}$ with the aid of the vibrational energy data for the bands.[9] A comparison of the ΔF's calculated from Eqs. (5a) and (5b) with the experimental values is given in Table IV. If you let $\epsilon=0.55$, the calculated ΔF's agree perfectly at $m=5$, but then they are higher for lower m's and lower for values of $m>5$ than the observed values. It is to be concluded that the observed data for these bands cannot be accurately fitted to the Kramers and Pauli formula after the fashion of Eqs. (5). A much better fit is obtained with Eqs. (6) below.

As indicated in Table I, the term $m=1$ is observed. We have re-examined our plates to verify this point and are quite certain that these two lines really are present. Granting that $m=1$ exists, j could not be taken equal to $(m-1)$ as we have done above,[10] without violating the necessary relation $j^2 \geqq \sigma^2$. We therefore put j equal to $m-\frac{1}{2}$ and $m+\frac{1}{2}$ for the low and high frequency components respectively with the following results:

Low-frequency components:

$$F'(m) = 6.00[\{(m-\tfrac{1}{2})^2-(\tfrac{1}{2})^2\}^{1/2}+0.11]^2-.000336[\quad]^4 \quad (6a)$$

$$F''(m) = 5.70[\{(m-\tfrac{1}{2})^2-(\tfrac{1}{2})^2\}^{1/2}+0.02]^2-.000332[\quad]^4 \quad (6b)$$

High-frequency components:

$$F'(m) = 6.00[\{(m+\tfrac{1}{2})^2-(\tfrac{1}{2})^2\}^{1/2}-0.89]^2-.000336[\quad]^4 \quad (6c)$$

$$F''(m) = 5.70[\{(m+\tfrac{1}{2})^2-(\tfrac{1}{2})^2\}^{1/2}-0.98]^2-.000332[\quad]^4 \quad (6d)$$

These expressions yield ΔF's which agree much better with the observed values than do those from Eqs. (5), as will be seen from the

[8] Kratzer, Ann. d. Physik **71**, 72 (1923).

[9] W. W. Watson, Phys. Rev. **27**, 801 (1926).

[10] Kratzer (Zeits. f. Physik **23**, 298 (1924)) lets $j=m-1$ for the CH bands, but since he did not observe the lowest terms, he did not encounter this question.

comparison of the observed and calculated ΔF's for values of m up to 10 given in Table IV. Eqs. (6) do not represent the data exactly for

TABLE IV

Comparison of values of $\Delta F'$ and $\Delta F''$ calculated from Eqs. (5a) *and* (6a) *with observed values.*

m	$\Delta F'(m)$ Calc. from (5a)	$\Delta F'(m)$ Calc. from (6a)	Obs.	$\Delta F''(m)$ Calc from (5b)	$\Delta F''(m)$ Calc. from (6b)	Obs.
2	———	39.22	39.30	34.18	34.75	35.02
3	64.93	62.66	62.41	56.95	57.42	57.43
4	84.73	86.54	86.10	79.68	80.14	80.16
5	108.18	110.39	110.00	102.35	102.80	102.90
6	31.81	34.16	33.97	24.94	25.40	25.67
7	55.44	57.86	57.94	47.45	47.91	48.32
8	78.99	81.45	81.78	69.86	70.32	70.84
9	202.45	204.91	205.38	92.15	92.60	93.45

the highest values of m. The reason appears from the fact that the fourth power term in the energy expression yields values of $\Delta^3 F(m)$ which are linear in m, whereas the experimental values of Table II are practically independent of m for the higher terms, suggesting the presence of an appreciable third power term in the energy expression.

It seems probable, then, that for the MgH bands the j's have half-integral values, the minimum values of both j' and j'' being $\frac{1}{2}$. The probable values of the electronic quantum numbers are $\sigma' = \frac{1}{2}$, $\sigma'' < \frac{1}{2}$ (very small, judging from the linear course of the ΔF's), and $\epsilon' \cong \epsilon'' \cong 0$. This being the case, it is apparent that these bands resemble more the ZnH bands than they do the CH bands, and consequently they are not to be classed with the latter bands in the table of structure types.

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EXCITATION OF SPECTRA BY ATOMIC HYDROGEN

By F. L. Mohler

Abstract

Spectroscopic excitation of Na, K, Cs, Mg, Cd, Zn, Hg, Tl vapors by atomic hydrogen.—Hydrogen from a Wood discharge tube flowed into a tube containing metal vapor and the spectrum emitted by the mixture was observed. Sodium and cadmium gave strong emission of their first resonance lines and no other lines. Potassium showed the first resonance doublet faintly. Mercury gave the complete hydride spectrum and faint emission of λ2537. Caesium, magnesium, thallium and zinc gave no line spectra.

Theory of excitation of spectra by atomic hydrogen.—Two possibilities are suggested. A three body collision of two hydrogen atoms and a metal atom may result in recombination of the hydrogen and excitation of the metal atom. A metal hydride may first be formed and this in a two body collision with a hydrogen atom may react to give H_2 and an excited metal atom. The available energy of excitation is somewhat less in the second case.

Introduction

R. W. WOOD[1] has found that hydrogen may be almost completely dissociated when a powerful discharge is maintained in a long tube through which moist hydrogen is streamed. The high degree of dissociation is indicated by the fact that, in the middle portion of the tube, only the atomic lines (Balmer series) can be seen. If the gas is pumped off from near the center of the tube the atomic hydrogen may be drawn some distance from the discharge, for its life is of the order of 0.3 sec. under favorable conditions. Wood[2] and Bonhoeffer[3] have studied many of the physical and chemical properties of atomic hydrogen by this means. Their results indicate that the successful operation of the discharge tube depends on the fact that the smooth clean surface of a glass tube exposed to water vapor or oxygen is unable to catalyse the recombination of hydrogen while almost any other solid surface is an effective catalytic agent.

Bonhoeffer[4] has obtained some experimental results on spectra excited when other gases, particularly metal vapors, are mixed with the atomic hydrogen. The foreign substance is introduced at some distance from the discharge tube to avoid any question of electrical excitation and the spectrum is observed near the point where the gases mix. This is a very interesting case of chemical luminescence and in view of the fact that some of his results are quite unexpected it seemed

[1] Wood, Proc. Roy. Soc. **97**, p. 455 (1920).
[2] Wood, Proc. Roy. Soc. **102**, p. 1 (1923).
[3] Bonhoeffer, Zeits. f. Phys. Chem. **113**, p. 199 (1924): **119**, p. 385 (1926).
[4] Bonhoeffer, Zeits. f. Phys. Chem. **116**, p. 391 (1925).

worth while both to repeat his experiments and to extend the method to other metals. Details of his results will be given in connection with the present observations.

Experimental Procedure

Fig. 1 illustrates the experimental arrangement used. Hydrogen was supplied by an electrolytic generator kept in continuous operation with a current of one or two amperes. The gas passed through a long

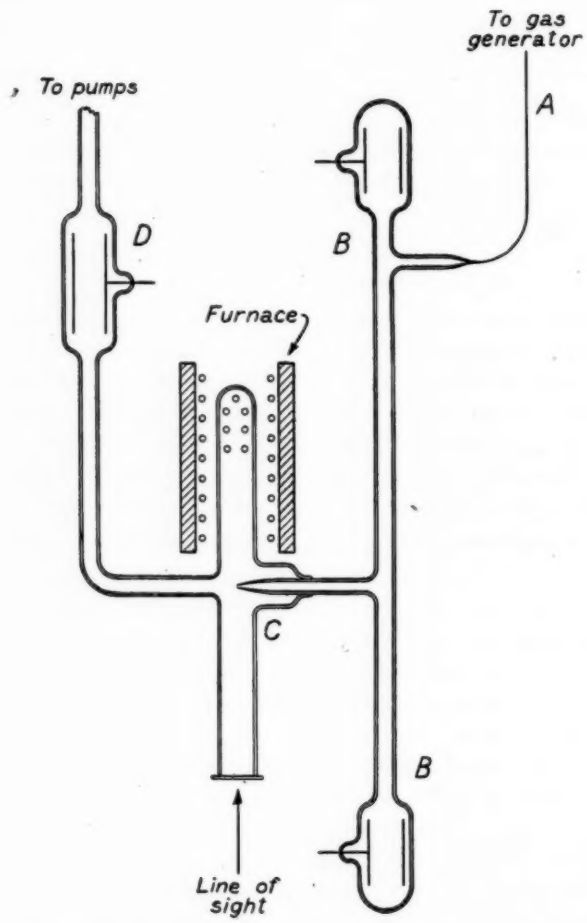

Fig. 1. Apparatus for excitation of metal vapor by atomic hydrogen.

capillary tube A into the discharge tube B, thence into the mixing chamber C, and from C was drawn off through a series of pumps. The discharge tube was about 150 cm long and 1.5 cm in diameter. The

mixing chamber was a tube about 2 cm in diameter into which the hydrogen flowed through a nozzle 1 mm in diameter at the tip. One end of this tube contained metal which could be heated by an electric furnace while the other end was closed by a quartz window through which the radiation could be observed.

The discharge was excited by a 5,000 volt transformer giving about 0.5 amps. in the secondary. The gas pressure was between 0.1 and 0.05 mm, corresponding to a gas flow of about 1,000 cc per second. Under these conditions there is no tendency for the discharge to pass into the tube between B and C nor for the vapor to diffuse into tube B. An auxiliary electrode D made it possible to draw a discharge through the mixing chamber when desired. Spectrum observations of this discharge gave useful information as to the composition of the gas mixture in C. Visual observations of the spectrum of the discharge in B indicated whether the operation of the tube was satisfactory. The metal in the mixing chamber was usually heated by an electric furnace to a temperature sufficient to give a vapor pressure comparable with the gas pressure, approximately 0.1 mm. Mercury however was heated enough by the atomic hydrogen to give a high vapor pressure.

In the first experiments with sodium, the mixing chamber was a simple cross with sodium in one arm and hydrogen passing through the two perpendicular arms. When the tube was first heated there was a brilliant yellow glow where the gases mixed but this soon faded. The trouble was that sodium or sodium compounds contaminated the tube between B and C so that rapid surface recombination took place. This was evidenced by the fact that dirty spots became very hot. The device shown in Fig. 1, with hydrogen entering through a small nozzle, reduced to a minimum the back diffusion of impurities and made it possible to maintain a bright glow for over twelve hours. Nevertheless contamination of the tubing is the most serious source of difficulty in these experiments. The mixing tube was cleaned after every run and the entire apparatus was frequently cleaned and sections of new tubing put in. Spectra were photographed with a Hilger E_2 quartz spectrograph.

Observations

Sodium. A diffuse yellow glow became conspicuous at about 200°C. This became much brighter and concentrated near the nozzle at higher temperature. The optimum temperature for long exposures was about 350°C. Both dicyanine stained plates and Speedway plates were used to secure maximum sensitivity to infra-red and ultra-violet lines, but exposures up to twelve hours showed only the D lines. Rough comparison exposures were made with a sodium flame and a discharge through the mixing chamber. The lines near 8190A and 3300A, if

present at all, were weaker relative to the D lines in the mixture than in the flame, enormously weaker than in the discharge. The results confirm Bonhoeffer's observations[4] with additional evidence as to the infra-red region.

Potassium, rubidium and caesium. Bonhoeffer[4] concluded that no visible lines of these metals were excited. With rubidium and caesium a blue light was observed over the surface of the metal, the spectrum being apparently continuous. In the present work, potassium heated to about 250°C was photographed with dicyanine stained plates and with unstained plates. A twelve hour exposure showed only the first doublet of the principal series 7665–99A, and this very faintly. Caesium when first exposed to the hydrogen, showed the surface fluorescence described by Bonhoeffer, but the effect was transient. A four hour exposure with a stained plate, and with caesium maintained at about 200°C, showed nothing.

Magnesium, heated to 600°C, showed no lines either visually or on a Speedway plate. I conclude that the resonance line $1^1S-2^3P_1$ at 4571A was definitely absent. A transient green surface fluorescence was observed when magnesium in powder form was put in the tube.

Cadmium, heated to about 350°C, gave the resonance line $1^1S-2^3P_1$ at 3261A in great intensity. A ten hour exposure showed the line much widened by over-exposure. No other lines or bands were seen.

Zinc was heated to about 440°C and a seven hour exposure showed nothing. The first resonance line is in this case at 3076A. Several check observations confirmed the fact that this line was absent under conditions which gave strong excitation of the cadmium resonance line.

Mercury. The spectrum excited in the presence of mercury vapor has been photographed by Bonhoeffer,[4] who found the mercury hydride bands strongly excited and the resonance line at 2537A present but faint. My observations confirm this. The mercury is warmed by the stream of atomic hydrogen until rapid evaporation takes place, and then a violet glow is visible. A ten hour exposure showed nearly all the known mercury-hydride bands and 2537. The band spectrum which extends from 4520 to 3270A has been analyzed in detail[5] and can safely be ascribed to a diatomic molecule HgH which is very unstable.

Thallium. Visual observation showed no luminosity when the metal was heated to 600°C which gives definite evidence of the absence of the green line $2^2P_2-2^2S$ at 5350A.

Water vapor. Water vapor is always present under the conditions of the experiment and the water band at 3064A, ascribed to OH, is emitted in the atomic hydrogen stream. The presence of metal vapor suppressed this afterglow.

[5] Hulthèn, Zeits. f. Physik. **32**, p. 32 (1925).

Table I summarizes the spectrum observations and gives the excitation potentials of the observed lines and of other significant lines which seemed to be definitely absent. There would seem to be no simple correlation between the occurrence of the lines and their excita-

TABLE I

Spectra excited by atomic hydrogen.

Element	Wave-length	Series	Excit. Pot.	Intensity
Na	5890–6	$1S$–$2P$	2.1	strong
	8183–94	$2P$–$3D$	3.6	absent
	3302–3	$1S$–$3P$	3.7	absent
K	7665–99	$1S$–$2P$	1.6	weak
	4044–7	$1S$–$3P$	3.0	absent
Cs	All lines		1.4 to 3.9	absent
Mg	4571	1^1S–2^3P_1	2.7	absent
Cd	3261	1^1S–2^3P_1	3.8	strong
Zn	3076	1^1S–2^3P_1	4.0	absent
Hg	2537	1^1S–2^3P_1	4.9	weak
HgH	4520 to 3274	Bands	3.1 to 3.8	strong
Tl	5350	2^2P_2–2^2S		absent

tion voltage. With the exception of the mercury line at 2537A, all the observed lines and bands have excitation potentials less than 3.9 volts, though many lines with lower excitation potentials did not appear. The absence of hydride spectra, except in mercury, is also interesting, for zinc, cadmium and magnesium have hydride spectra quite similar to that of mercury.

INTERPRETATION OF RESULTS

The various experiments on the properties of hydrogen drawn from a Wood tube clearly indicate that atomic hydrogen is the active agent. The relatively long life of the atoms can be explained by assuming that two atoms cannot spontaneously recombine to form a molecule, and theoretical considerations support this assumption. The process of recombination is to be considered as a special case of changing from one vibration state to another and, in the normal electronic state, the vibration states of homopolar molecules are metastable.[6] Hence two atoms cannot radiate away the energy of recombination, and some third body must be present to take up this energy. A possible explanation of spectrum excitation by atomic hydrogen is that a three body collision of two hydrogen atoms and a metal atom takes place in which part of the energy of recombination is expended in producing excitation of the metal atom. The process is the converse of the Franck and Cario experiment in which H_2 is dissociated by optically excited mercury vapor.[7]

[6] Birge and Sponer, Phys. Rev. **28**, p. 259 (1926).

[7] Franck and Cario, Zeits. f. Physik. **11**, p. 161 (1922).

Miss Sponer[8] has explained the afterglow spectra of pure nitrogen and of mixtures of nitrogen and other gases on the assumption that active nitrogen is atomic nitrogen which recombines only by three body collisions. The energy of recombination, 11.5 volts, is sufficient to excite the complete arc spectra of all metal vapors though there is evidence that all lines do not appear in their normal intensity.[9]

The work of dissociation of hydrogen can be directly measured, though with difficulty, from the amount of dissociation at high temperature. Values so obtained range from 3.7 to 4.2 volts.[10,11] A more certain value is derived from the band spectrum by assuming that the limiting value of the vibration energy of the normal electronic state is equivalent to the work of dissociation. Witmer[12] has derived a value 4.34 volts from one series in the Schumann region, and a more complete analysis of the H_2 spectrum by Dieke and Hopfield[13] gives 4.38 volts.

The simplest assumption as to the excitation of other atoms by atomic hydrogen is that any atomic states of energy less than the energy of recombination can be excited in a three body collision. My results show that this is not the case. Thus in cadmium the state 2^3P_1 of energy, 3.8 volts is strongly excited while in sodium the state 3^2P of energy, 3.7 volts is not excited. The strong emission of the *D* lines shows that in this comparison there is no question of contamination of the tube suppressing radiation. Particular care was taken to maintain comparable conditions in the experiments with zinc and cadmium and it may be that zinc is not excited because the energy of recombination is insufficient. This would mean that it is less than 4 volts, a value definitely at variance with the band spectrum results. In view of the existence of an unknown factor preventing the excitation of some states, the evidence for a low value is not conclusive.

The excitation of the mercury hydride spectrum can be explained by assuming that first HgH is formed and that then the hydride is excited in a three body collision. The energy of recombination of HgH is very small (Hulthèn[5] estimates it at 0.37 volts on the basis of the observed vibration states) so that no visible radiation can result from its formation. Probably the reaction between Hg and H takes place at the liquid mercury surface. (Bonhoeffer).[4] The hydrides of the other metals studied are also very unstable, and the energy involved in their formation cannot give atomic spectrum excitation. Possibly

[8] Sponer, Zeits. f. Physik. **34**, p. 622 (1925).
[9] Ruark, Foote, Rudnick and Chenault, J.O.S.A. & R.S.I., **14**, p. 17 (1927).
[10] Langmuir, J. Amer. Chem. Soc., 38, p. 221, 1916.
[11] Isnardi, Zeits. f. Elektro. Chem. 30, p. 405 (1915).
[12] Witmer, Proc. Nat. Acad. Sci. 12, p. 238 (1926).
[13] Dieke and Hopfield, Zeits. f. Physik., in press.

the failure to observe hydride spectra except in mercury is explained by the fact that the higher temperatures and lower pressures employed prevented the existence of any appreciable concentration of these unstable compounds.

There is a possibility however that hydride formation plays an essential part in all the reactions. Suppose that first a metal hydride XH is formed (possibly at a solid or liquid surface) involving a heat of reaction Q_{XH} and that subsequently an atom of hydrogen reacts with XH to form H_2 and an excited atom X′ of energy $Q_{X'}$

$$H+XH \rightarrow H_2+X'+Q_{H_2}-Q_{XH}-Q_{X'}$$

This reaction will take place if $Q_{X'}<Q_{H_2}-Q_{XH}$. Q_{XH} is small yet the small difference will account for the nonappearance of lines near the threshold value. Occurrence of line emission will depend on the existence of the hydride as well as on the available energy. This hypothesis seems to account for the observations on line spectrum excitation but it does not offer a simple explanation of the HgH bands. Possibly the primary product is in this case HgH_2, though chemical evidence as to the existence of such a compound is questionable.

Neither theory accounts for the excitation of the mercury line at 2537A. The energy required, 4.9 volts, is much more than the available energy from recombination and some multiple excitation process must be involved.

BUREAU OF STANDARDS,
December 20, 1926.

MULTIPLETS IN TWO ELECTRON SYSTEMS OF THE FIRST LONG PERIOD*

By R. C. Gibbs and H. E. White

Abstract

Wave-lengths and comparative positions of certain multiplets in the spectra of Ca_I, Sc_{II}, Ti_{III}, V_{IV}, Cr_V.—When an electron in a $4p$ orbit jumps to a $4s$ orbit in the presence of another valence electron in a $3d$ orbit, multiplets of the type $^3D_{1,2,3}-{}^3P_{0,1,2}$; $^3D_{1,2,3}-{}^3D'_{1,2,3}$; $^3D_{1,2,3}-{}^3F_{2,3,4}$ appear. These multiplets for Ca_I, Sc_{II}, Ti_{III} have already been recognized by other investigators. The same multiplets for V_{IV} and Cr_V have now been found and the wave-lengths of the lines have been measured. The progressive shift in the relative positions of these multiplets in passing from element to element has been noted. The *regular and irregular doublet laws* have been found to hold fairly accurately for two electron systems when one of the electrons jumps between two orbits, p and s, having the same total quantum number.

ACCORDING to the new theory of space quantization a single valence-electron gives rise to a system of doublet levels. In the presence of another valence-electron, however, the doublet levels are replaced by singlet and triplet levels, except when both electrons are in s orbits having the same total quantum number. These triplet levels in general give rise to groups of lines called multiplets.

Ca_I, Sc_{II}, Ti_{III} etc., each contains two valence electrons and we should therefore expect to find such multiplets in their spectra and also that each of the three multiplets would have somewhat the same structure for all these atoms.

The Ca_I spectrum is known from the work of Russell and Saunders,[1] in which they find the lowest level to be a $^1S_0$ level. This $^1S_0$ level is the resultant of two similar (s) electrons in orbits of total quantum number 4, the normal state of the atom. When one of these (s) electrons is excited to a $3d$ orbit, the two electrons will then give rise to $^1D_2$ and $^3D_{1,2,3}$ levels. If the other (s) electron is now displaced to a $4p$ orbit, the two electrons, one in a $3d$ orbit and the other in a $4p$ orbit, will give rise to $^1P_1$, $^1D'_2$, $^1F_3$, $^3P_{0,1,2}$, $^3D'_{1,2,3}$, $^3F_{2,3,4}$ levels. When the electron in the $4p$ orbit returns to the lower $4s$ orbit there will result radiations corresponding to jumps from any one of the $^1P_1$, $^1D'_2$, $^1F_3$, $^3P_{0,1,2}$, $^3D'_{1,2,3}$, $^3F_{2,3,4}$ levels to any one of the $^1D_2$ or $^3D_{1,2,3}$ levels except those excluded by the selection principle ($\Delta j=0, \pm 1$). The jumping

* The assistance of a grant to the first author from the Heckscher Research Foundation of Cornell University which enabled us to obtain the results described in this report is gratefully acknowledged.

[1] H. N. Russell and F. A. Saunders, Astrophys. J. **61**, p. 38 (1925).

of one electron from the $4p$ orbit to the $4s$ orbit, the stationary state of the other valence electron in the $3d$ orbit remaining unchanged, will correspond exactly to the jumps in the one electron systems[2] except that here it is jumping in a field which is modified by the presence of another electron in a $3d$ orbit. This causes not only a shift in the radiated frequency but an increase in the number of lines radiated.

Scandium in the normal state contains three valence electrons, two of them are in s orbits and the other in a d orbit, the latter being more tightly bound than either of the (s) electrons. If now an electron be removed from the normal scandium atom it will probably be one of the (s) electrons which is ejected. The two remaining electrons should then give rise to $^1D_2$ and $^3D_{1,2,3}$ levels as the lowest state in the first spark spectrum of scandium, with the $^3D_{1,2,3}$ according to Hund,[3]

TABLE I

Titanium (III) triplets. (H. N. Russell).

		a^3D_3		a^3D_2		a^3D_1
		361.69	(227.2)	134.48	(134.5)	000
		9		1		
		2564.17		2549.32		
$a^3D'_{1,3}$	39360.7	38999.0		39226.2		
	(257.6)	7		8		5
		2581.21		2566.16		2557.35
$a^3D'_2$	39103.1	38741.5		38968.7		39103.0
	(166.9)			6		7
				2577.22		2568.29
$a^3D'_{3,1}$	38936.2			38801.5		38936.4
		10				
		2516.76				
a^3F_4	40095.4	39733.7				
	(412.7)	2		9		
		2543.17		2528.56		
a^3F_3	39682.7	39320.9		39548.2		
	(324.7)	0		2		8
		2564.36		2549.45		2540.78
a^3F_2	39358.0	38996.0		39224.1		39357.9
		8		3		0
		2347.50		2335.05		2327.75
a^3P_2	42959.8	42598.5		42825.7		42959.8
	(85.3)			5		1
				2339.73		2332.39
a^3P_1	42874.5			42740.0		42874.5
	—(5.9)					3
						2332.07
a^3P_0	42880.4					42880.4

[2] R. C. Gibbs and H. E. White, Proc. Nat. Acad. Sci. **12**, p. 448 (1926); **12**, p. 675 (1926).

[3] Hund, Zeits. f. Physik **33**, p. 345 (1925).

lying deeper than the $^1D_2$ level. If now the (s) electron is displaced to a $4p$ orbit, and the (s) electron is indeed more free to move than the (d) electron, we again get $^1P_1$, $^1D'_2$, $^1F_3$, $^3P_{0,1,2}$, $^3D'_{1,2,3}$, $^3F_{2,3,4}$ levels.

Similarly, Ti_{III}, V_{IV} etc., will give these same types of levels when two, three, etc., valence electrons have been removed respectively, giving as before $^1D_2$ and $^3D_{1,2,3}$ as the lower levels, when one electron is in a $3d$ orbit and the other is in a $4s$ orbit, and $^1P_1$, $^1D'_2$, $^1F_3$, $^3P_{0,1,2}$, $^3D'_{1,2,3}$, $^3F_{2,3,4}$ levels when the (s) electron has been displaced to a $4p$ orbit.

TABLE II

Vanadium (IV) triplets.

		a^3D_3 600.4	(385.0)	a^3D_2 215.4	(215.4)	a^3D_1 000
		6		1		
		1997.74		1982.49		
$a^3D'_1$	50656.9	50056.6		50441.6		
	(424.6)	5		5		3
		2014.83		1999.32		1990.75
$a^3D'_2$	50232.3	49632.0		50017.0		50232.3
	(310.2)			2		4
				2011.80		2003.12
$a^3D'_3$	49922.1			49706.7		49922.1
		6				
		1939.07				
a^3F_4	52171.4	51571.1				
	(712.9)	0		6		
		1966.25		1951.48		
a^3F_3	51458.5	50858.2		51243.1		
	(519.5)	0		1		6
		1986.54		1971.47		1963.13
a^3F_2	50939.0	50338.8		50723.6		50939.0
		8		6		4
		1845.09		1832.07		1824.91
a^3P_2	54797.2	54197.9		54583.1		54797.2
	(83.2)			5		1
				1829.28		1822.10
a^3P_1	54880.4			54666.3		54881.7
	(140.8)					4
						1817.48
a^3P_0	55021.2					55021.2

The lines caused by transitions from the $^3P_{0,1,2}$, $^3D'_{1,2,3}$, $^3F_{2,3,4}$ states to the $^3D_{1,2,3}$ states are characteristic multiplets of which $^3D_{1,2,3}-{}^3D'_{1,2,3}$ is the easiest to recognize by its somewhat symmetrical configuration. This multiplet is composed of seven lines, while the other two $^3D_{1,2,3}-{}^3P_{0,1,2}$ and $^3D_{1,2,3}-{}^3F_{2,3,4}$ are made up of six lines

each. These multiplets in Ca_I are given by Russell and Saunders[1] in the visible region of the spectrum, and those for Sc_{II} by Meggers[4] in the ultra-violet region. Dr. Russell has very kindly put at our disposal his unpublished data of the corresponding multiplets of Ti_{III}. These three multiplets are given in Table I, with the relative term values of the levels, where the value of the $^3D_1$ level is taken as zero. The intensities of the Ti_{III} lines are taken from our own photographs of these multiplets. The first two multiplets of V_{IV} recorded in Table II occur at the threshold of the air absorption limit of the ordinary grating spectrograph. The other multiplet, $^3D_{1,2,3}-{}^3P_{0,1,2}$ of V_{IV} as well as all three multiplets of Cr_V lie still deeper in the ultra-violet and were obtained from plates very kindly taken for us by Dr. I. S. Bowen of the California Institute of Technology using a vacuum spectrograph.

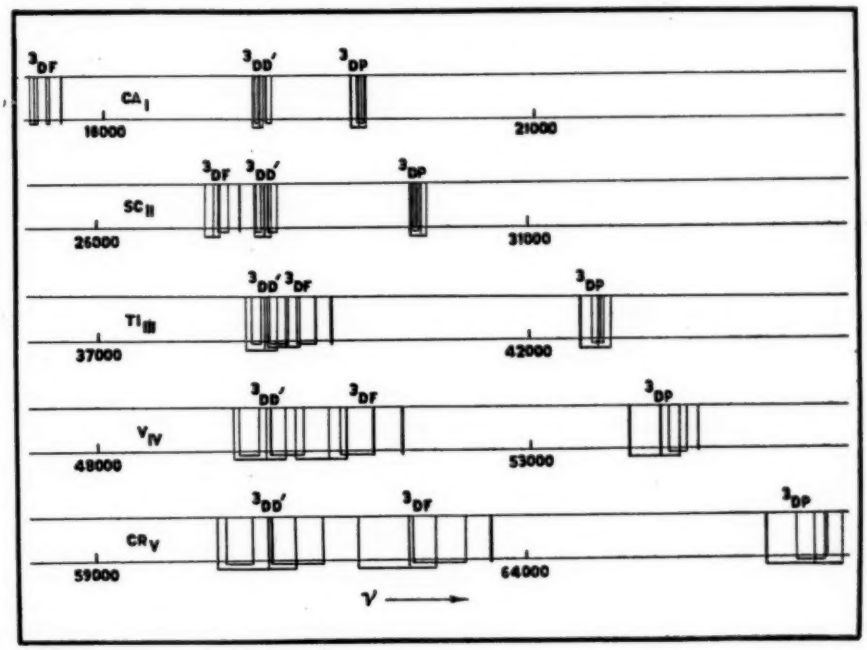

FIG. 1. Relative positions of multiplets.

Since we are here dealing with lines arising from an electron transition between orbits of the same total quantum number they would be expected to follow the irregular doublet law just as was found to be the case for the doublets of these elements[2] when their atoms contain only *one* valence electron. Fig. 1 is given for the purpose of showing the

[4] Meggers, Journal Wash. Acad. Sci. 14, p. 419 (1924).

application of the irregular doublet law to each group of lines, i.e. the almost linear progression of ν with increasing atomic number, as well as the relative shifting of the ^3DF and ^3DP multiplets with respect to the $^3DD'$ multiplet. It may be seen that the ^3DF and $^3DD'$ groups progress very regularly while the ^3DP group shows small irregularities in going from element to element.

TABLE III

Chromium (V) triplets.

		a^3D_3 912.0	(596.7)	a^3D_2 315.3	(315.3)	a^3D_1 000
		6		0		
		1638.51		1622.64		
$a^3D'_1$ 3	61943.6	61031.0		61628.0		
	(630.0)	2		5		1
		1655.60		1639.40		1630.96
$a^3D'_2$	61313.6	60401.0		60997.9		61313.6
	(488.2)			2		4
				1652.63		1644.05
$a^3D'_3$ 1	60825.4			60509.5		60825.4
		7				
		1573.16				
a^3F_4	64477.9	63566.3				
	(895.5)	1		4		
		1595.64		1580.62		
a^3F_3	63582.4	62670.8		63266.3		
	(633.5)	?		2		2
		(1611.95)		1596.59		1588.57
a^3F_2	62948.9	62036.7		62633.5		62948.9
		8		5		0
		1497.97		1484.67		1477.75
a^3P_2	67669.7	66757.0		67355.0		67670.2
	(230.2)			6		3
				1489.75		1482.81
a^3P_1	67439.5			67125.3		67439.5
	— (51.4)					5
						1481.68
a^3P_0	67490.9					67490.9

The regular doublet law, derived by Sommerfeld[5] from relativity considerations and by Heisenberg and Jordan[6] from the new quantum mechanics of the spinning electron, shows not only that the value of $(\Delta\nu)^{1/4}$ should be a linear function of Z, but that $\Delta\lambda$ should remain nearly constant for increasing atomic number. These laws are found

[5] Sommerfeld, Atombau, 4th German edition 1924, p. 144.
[6] W. Heisenberg and P. Jordan, Zeits. f. Physik, **37**, p. 276 (1926).

to hold even in these triplet systems except for possibly the Car multiplets. The values given in Table IV show how beautifully these relations are fulfilled. Using the same constant in Sommerfeld's

TABLE IV

Regular doublet law
$\Delta_1\lambda = (a^3D_3 - a^3D'_3) - (a^3D_2 - a^3D'_2)$
$\Delta_2\lambda = (a^3D_3 - a^3D'_2) - (a^3D_1 - a^3D'_2)$

Element	$\Delta\nu$ $a^3D_3 - a^3D_2$	$(\Delta\nu/.0456)^{1/4}$	s	$\Delta_1\lambda$	$\Delta_2\lambda$
CaI	21.9	4.681	15.32	6.63	12.43
ScII	109.97	7.008	13.99	13.98	17.95
TiIII	227.2	8.400	13.60	14.85	17.04
VIV	385.0	9.585	13.41	15.25	17.09
CrV	596.9	10.696	13.30	15.87	17.09

relativity formula as is used for doublets of the same period[2] the screening constants are found for every element to be larger, by a very nearly constant value, than they are for the corresponding one electron systems which is the effect to be expected from the addition of one more valence electron.

In these two electron systems it is found that the observed frequencies appear at very nearly the same region of the spectrum as do the corresponding doublets of the one electron systems in this same period.[2] This relation is shown in Table V using the $4^2S_1 - 4^2P_1$ line in the doublet

TABLE V

Shift due to the presence of a second valence electron.

	Doublets $4^2S_1 - 4^2P_1$		*Triplets* $a^3D_3 - a^3F_4$	*Diff.*
CaII	25191.6	CaI	15525.9	9665.7
ScIII	36565.3	ScII	27663.6	8901.7
TiIV	47533.3	TiIII	39733.7	7799.6
V V	58249.9	VIV	51571.4	6678.5
CrVI	68713.8	CrV	63566.3	5147.5

systems and the $a^3D_3 - a^3F_4$ line in the triplet systems. The consistently larger frequencies of the doublets as compared with those of the triplets suggests that this shift in frequency from one system to the other is caused by the screening effect of an additional electron, in this case an electron in a $3d$ orbit.

One of the irregular doublet laws requires that the value of $\Delta(\nu/R)^{1/2}$ be a constant for the corresponding term values of the stationary states between which a transition is taking place. The only term values known are those given by Russell and Saunders[1] for CaI. The term values used to obtain the Moseley diagram Fig. 2 are merely extrapolated

values computed from the known values of the first element Ca_I, the slope of the extrapolated curve for $(\nu/R)^{1/2}$ being so chosen as to yield a similar line for other levels when these other levels are obtained by adding or subtracting the observed frequencies of radiation from those of the extrapolated levels. Although these extrapolated term values may differ somewhat from their true values, yet the figure shows very well the way in which the different levels are changing in going from element to element, and when once started, serves as an aid in predicting the approximate positions of new lines.

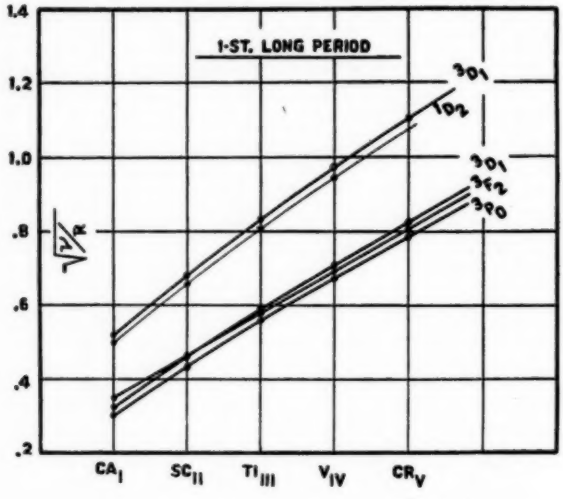

FIG. 2. Moseley diagram.

We have here been dealing with two valence electrons, the initial state of the atom having one electron in a $4p$ orbit and the other in a $3d$ orbit. The final state finds one electron in a $4s$ orbit and the other in a $3d$ orbit. It is interesting to note that this electron transition may take place in two ways, either one electron is jumping from a $4p$ to a $4s$ orbit, the $3d$ electron remaining fixed, or two electrons are jumping, one from a $4p$ orbit to a $3d$ orbit and the other from a $3d$ orbit to a $4s$ orbit. In the latter case one electron is changing by $k=1$ and the other by $k=2$ which is in accordance with the usual quantum conditions of two electron jumps.[7] The sum of the total quantum numbers is the same in either of the above mentioned cases.

CORNELL UNIVERSITY,
November 10, 1926.

[7] W. Heisenberg, Zeits. f. Physik, 32, 841 (1925).

ON ELECTRON SCATTERING IN HELIUM

By E. G. Dymond

Abstract

Velocity and angular distribution of electrons scattered by single collisions in helium.—An apparatus is described in which both the velocity and the angular distribution of electrons which have suffered single collisions in a gas are examined. It is found in helium that, for initial velocities of 100 volts and over, the principal energy loss is due to the excitation of the 2^1S state, corresponding to 20.5 volts. No loss corresponding to 19.7 volts is found for these velocities. For still higher velocities it seems probable that the energy interchange ceases to be quantized, and that the atom is capable of absorbing temporarily more energy than is required for excitation. The angular distribution of electrons which have lost 20.5 volts energy in colliding shows very marked maxima, the predominant one being in the forward direction. The bearing of the Schrödinger wave mechanics on this point is discussed.

THE problems of electron collisions have been in the past attacked from only two sides; that is by the determination of critical potentials and of the efficiency of excitation and ionization. The information which we may obtain from these sources, useful as it has been, is, especially in the case of efficiency of inelastic impact, very incomplete, and also is insufficient in itself to provide us with an idea of the mechanism of excitation or ionization. We need in addition to the energetic relations of collisions, those of momenta also. We must consequently trace the paths of the colliding bodies as well as determine the interchange of energy between them.

Because of the disparity in the masses of the atom and the electron it is only necessary to follow the latter. Little work has been done in this field. Davisson and Kunsman[1] have investigated the scattering of electrons by thin metal films and Langmuir[2] has found some surprising features in the scattering on excitation in a gas.

In view of the unexpected results obtained by these workers and of the great theoretical interest recently attached to these phenomena the work to be described here was undertaken in order to determine with some exactness the angular distribution of the electron paths about the initial direction after a collision has taken place, and also to investigate the energy losses in a region of velocity which has hitherto been difficult of access. A brief report on the scattering has already been published.[3]

[1] Davisson and Kunsman, Phys. Rev. **22**, 242 (1923).
[2] Langmuir, Phys. Rev. **27**, 806 (1926).
[3] Dymond, Nature, p. 336, September 4, 1926.

Experimental Arrangements

A magnetic deflection method was used to determine the velocity distribution. The apparatus is shown in side and end elevations in Fig. 1. The source of electrons was a short tungsten filament surrounded by a copper cylinder A, whose end was closed by two discs pierced with two slits S_1. On the application of a field between cylinder and filament, this portion of the apparatus acted as a electron "gun." shooting out a narrow beam of electrons into the surrounding space. A glass tube supported the gun and received the leads from the filament and cylinder. This tube could be rotated about an axis BB, a ground sleeve C lubricated with rubber grease maintaining the airtightness of the whole. Immediately below the axis BB were two slits S_2 and S_3.

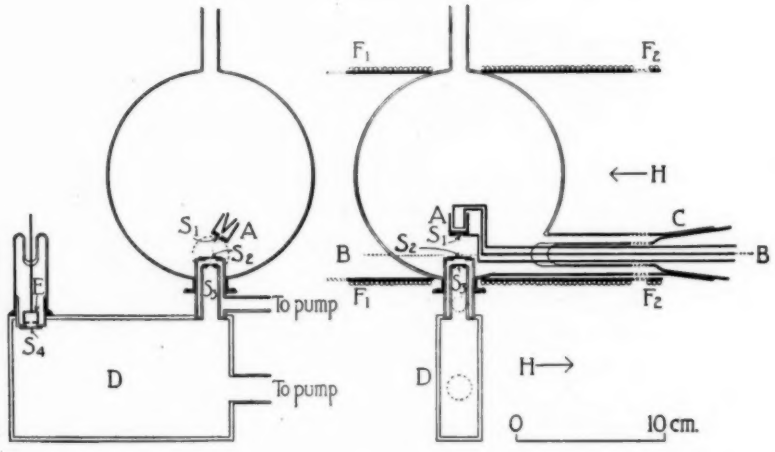

Fig. 1. Side and end elevations of apparatus.

It will be seen that these slits could select a group of electrons which had been scattered out of the main beam by collision with the gas anywhere along the line BB. By rotating the tube on which the gun is mounted the angle of scattering could be varied from 0° to 90°. By a suitable choice of gas pressures it was assured that electrons could pass through the slits S_2 and S_3 only after having made one collision.

After passing through S_3 the electrons were bent round in a magnetic field and received by the Faraday cylinder E through the slit S_4. By a device not shown, the width of S_4 could be adjusted while the apparatus was evacuated, a thin copper diaphragm being employed to take up the motion of the slit and to maintain gas tightness. A wide slit enabled feeble effects to be observed, while a narrow slit was required to separate groups of electrons of small velocity difference. Differences of velocity of 1 in 1000 could readily be detected. The

slits S_1 were 0.5 mm broad and 0.5 mm deep; S_2 was 0.1 mm broad and 0.9 mm deep; S_3 was 0.1 mm broad and V-shaped. S_4 was also V-shaped and could be varied from 2 mm to zero. All slits were 5 mm long. Two independent diffusion pumps of large capacity pumped off the gas leaking through S_2 and S_3 and maintained a low pressure in the interior of the brass velocity analyzing chamber D. This was necessary to prevent further scattering in this region. The error in the angle of scattering, due to electrons which do not travel in the plane of the paper (Fig. 1, side elevation), was not more than 1°, given by the ratio of the length of the slits to the length of path within the chamber D.

It will be noted that the magnetic field producing the deflection must not extend into the part of the apparatus where the collisions under consideration take place. As the determination of the velocity was made by varying the magnetic field and thus bringing electrons of different speeds on to the slit S_4, any field in the neighborhood of S_2 would by bending the primary electron stream vary the angle of scattering. A pair of coils in the Helmholtz arrangement (not shown) were used. They were sufficiently large to produce a sensibly uniform field over the whole of the apparatus; this field was compensated in the region comprising the gun A and slit S_2, by a pair of solenoids F_1 and F_2, carrying a fraction of the current through the main coils. The exact compensation was best effected by turning the gun to the vertical position, that is, corresponding to zero scattering angle, when there was no gas in the apparatus. The ratio of the currents through the two sets of coils was varied, until electrons were found to pass through the slit system and be received on E. The setting was found to be critical but did not require to be altered for different electron velocities, that is to say, for different magnetic fields. This method of compensation rendered the electron paths beneath the slits S_2 and S_3 far from circular, but as only comparative results for the velocities were required, this can raise no objection.

The helium, which was used throughout the research, was initially purified in a circulatory system by passing over heated copper oxide and charcoal cooled in liquid air. From the storage reservoir it could be passed into the apparatus through a fine capillary, passing again over cooled charcoal. Leaking through the slits S_2 and S_3, it was pumped off into another reservoir, and after repurification could be used again. The continual flow of gas made for purity, and in spite of the presence of a wax joint, joining the brass chamber to the glass part of the apparatus, and of the lubricated sleeve C, no trace of impurity was evident in the gas, as tested by the method later to be described. The current arriving at the Faraday cylinder E was measured by a Compton electrometer. It was frequently necessary to use the instrument at a sensitivity of 25,000 mm per volt. Except

for a steady drift of zero no difficulty was experienced in working at this sensitivity, until the onset of hot weather. The climate of New Jersey was then found unsuitable for further work on such small effects.

Discussion of Results

Due to the presence of three variables, the initial velocity of the primary beam, the velocity of the secondary scattered beam and the angle of scattering, the complete investigation is very lengthy and has not yet been made. It is felt however that the results already obtained may have sufficient interest to be reported now.

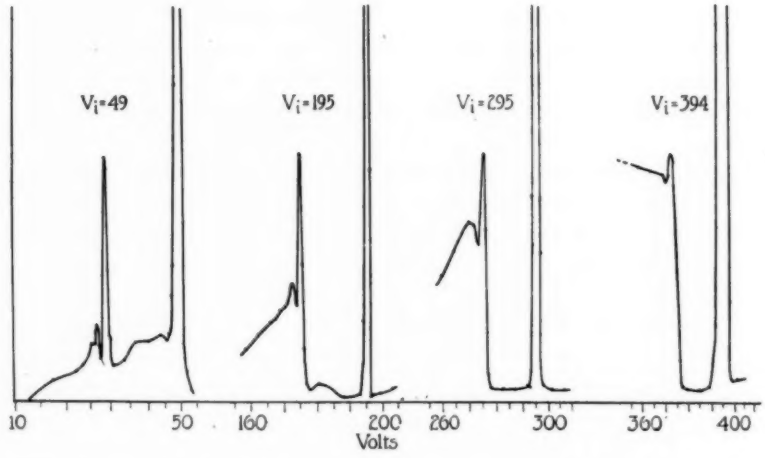

Fig. 2. Showing the relation of the number of electrons scattered by 5°, with their velocity for various initial velocities V_i.

We will first consider the velocity relations when the scattering angle is held constant. In the instances to be discussed, with one exception, this angle was 5°.

The results for a number of velocities, V_i, of the primary beam are collected in Fig. 2, where the ordinates represent the number of electrons scattered, and the abscissas are proportional to the magnetic field and consequently to the square root of the energy. The pressure of gas in all cases was 0.03 mm of mercury, except in those for which $V_i = 400$ volts, where it was 0.09 mm. Doubtless the broadening of the principal peak for those initial velocities was due to the higher gas pressure in the analyzing chamber D.

We notice in all cases two principal features, the presence of two peaks, one at a velocity equal to that of the primary beam, due to elastic reflection, and one some 20 volts lower, due to inelastic collisions which lead to excitation of the atom. The absence of any intermediate

peak speaks for the purity of the gas, if we except the run for $V_i = 50$, in which the liquid air surrounding the charcoal was low. There is also a smaller peak corresponding to large energy loss, constantly associated with the main one. The energy losses, calculated from the separation of the peaks is shown in Table I.

TABLE I

Energy losses of electrons in helium for various initial velocities V_i.

V_i	Energy losses (volts)		
49	19.7	20.7	22.6
97.6	——	20.8	23.2
196.	——	20.4	23.1
297.	——	20.4	24.2
395.	——	21.5	——
572.	——	22.0	——

For an initial velocity of 49 volts a slight hesitancy in the rise of the 20.7 volt peak may be interpreted as a loss of 19.7 volts energy. It is however very indistinct. It should correspond to the transfer $1^1S \rightarrow 2^3S$. The main peak is plainly due to the transfer $1^1S \rightarrow 2^1S$, which requires 20.55 volts. The mean value, determined from the first four rows is 20.58 volts. Lesser accuracy is to be expected for the higher initial velocities, as the loss of energy bears a smaller ratio to the initial energy.

The smaller peak is due to a complex of the higher states of helium, which are too close together to be resolved. Its behaviour is remarkable. With increase of initial velocity it gains in importance with respect to the 20.55 volt peak, and simultaneously broadens. By 400 volts initial velocity it forms a continuum which decreases very slowly with increasing energy loss and is perceptible to 200 volts.

It is possible that this continuum is due to ionization. As the electron ejected from the atom may have any velocity we should expect no sharp rise in the velocity distribution curve corresponding to a loss of 24.5 volts, a rise which in fact is never found. But if an electron loses say 200 volts in ionization, there should appear an electron of 175 volts energy, which has been ejected from the atom.

It seems that in fact there may be such an electron, if we look for it at scattering angles greater than 5°. Fig. 3 shows the scattering for an initial velocity of 340 volts and scattering angle 15°. A pronounced maximum at 50 volts has made its appearance, while the continuum afore mentioned rises to a maximum at about 290 volts. If we accept the view here given, there is a discrepancy of 25 volts in the expected positions of the two peaks. We can however form no complete picture of the processes involved without full knowledge of the behaviour of the curve shown in Fig. 3 for all angles. From the data already obtained

it appears that the maximum at 50 volts persists to large angles of scattering, while that in the neighborhood of 200 volts declines; the measurements are not yet sufficiently complete to show any periodic variation in intensity, as is the case with the peak due to excitation, to be discussed later.

It is difficult however to ascribe this continuum to ionization when we consider the relative intensities, for $V_i=50$ and $V_i=400$. For the lower velocity there is little or no evidence of any effect due to ionization, indicating that it is spread over a wide range of velocities. Now Compton and Van Voorhis[4] have shown that the efficiency of ionization

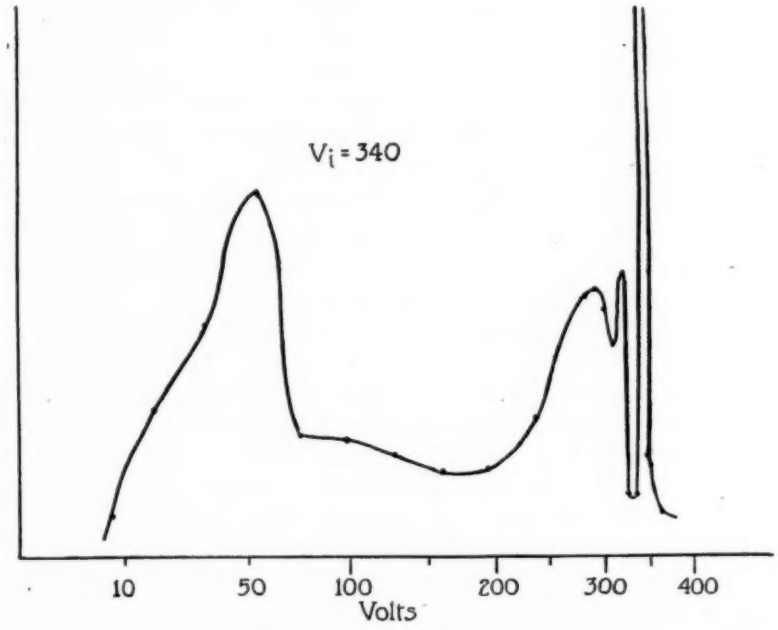

Fig. 3. Showing the number of electrons scattered by 15° for an initial velocity $V_i=340$.

in helium at 400 volts is only about twice its value at 50 volts. Further the continuum at the higher velocity does not begin at a point corresponding to an energy loss of 24.5 volts, but in the neighborhood of 22 volts.

Now for an electron whose speed is great compared with that of one of the orbital electrons of helium, the time of collision is short compared with the period of rotation in the orbit, or compared with the time required for quantization, if we speak in terms of the old quantum theory. No exact formulation of what this means when expressed in the new mechanics has been made, but a clue has been provided by

[4] Compton and Van Voorhis, Phys. Rev. **27**, 724 (1926).

Heisenberg,[5] who has reintroduced the idea of atomic frequencies. It is not unreasonable to expect therefore that when the time of collision is short compared with these frequencies (Resonanz-schwebungen) the normal laws of energy transfer break down, and that we may here admit the possibility that an electron may lose more energy to the atom than is necessary to cause transfer from one stationary state to another. A stable state would quickly be assumed by radiating the excess of energy, presumably in continuous radiation.

The continuum extending for energy losses greater than 22 volts is precisely what we should expect on this view.

It will be seen that when the series of curves shown in Fig. 2 is complete for all angles, the determination of the excitation probabilities will be an easy matter. The ratio of the heights of the subsidiary peaks to that due to elastic collisions, when integrated over all angles will give the excitation probabilities of the respective states. Except to note the absence of excitation to the first orthohelium state, requiring 19.7 volts, at the higher velocities, we can as yet make no certain statement on this point.

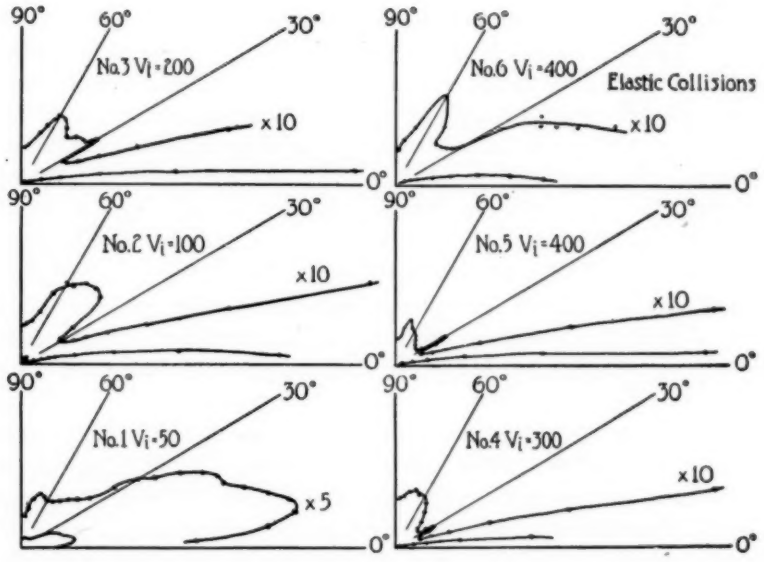

Fig. 4. Showing the number of electrons scattered at different angles for various initial velocities V_i. Nos. 1, 2, 3, 4 and 5 are for electrons which have lost 20.5 volts energy. No. 6 is for electrons which have lost no energy.

The Variation of Scattering with Angle

To determine the angular relations of the various types of collision it is only necessary to set the magnetic field to allow electrons with the

[5] Heisenberg. Zeits. f. Physik **38**, 411 (1926).

required energy loss to enter the Faraday cylinder and to rotate the electron gun A (Fig. 1).

A thorough investigation so far has only been undertaken for electrons losing 20.5 volts energy, that is to say, for those giving rise to the $1^1S \rightarrow 2^1S$ transition, for which $\Delta j = 0$. Fig. 4 shows the mean results of several runs at each angle. The radius vectors are proportional to the number of electrons scattered per unit solid angle at the various angles. The curves shown in my letter to Nature[5] are drawn from the same data, but represent the number scattered between two cones of semi-angles θ and $\theta + d\theta$. They differ from the curves here shown by a factor sin θ, which profoundly changes the relative intensities of the various maxima. It should be noted that Fig. 4 represents the original determinations, as of course the solid angle subtended by the slit S_2 at the point of impact is constant for all scattering angles.[6] The curves are reduced to have a common area, except where a multiplying factor indicates otherwise.

The principal maximum is found to move to smaller angles with increasing initial velocity. Above 100 volts it is too near zero to measure, but the rise increases in steepness at the higher velocities. The concentration of nearly all the electrons, which have excited at high velocities, in the forward direction is the effect already noted by Langmuir.[2] It should be noticed that as in the transition of the helium atom considered there is no change in the angular momentum ($\Delta j = 0$), the electron cannot pursue identical paths before and after collision, but one must be displaced parallel to the other (assuming that there is no deflection). For a collision in which $\Delta j = 1$, there is a unique striking radius for which the electron may pursue a straight path, but in general the path after collision will also be displaced laterally.

In addition to the maximum considered, in which all but a small fraction of the electrons lie, another maximum is found at larger angles, which moves with increasing initial velocity of the electron in the opposite direction, that is to say to greater angles.

Further, for velocities greater than 200 volts, there appears a peak, remarkable for its sharpness, which does not alter its position but increases in intensity with increasing velocity. The positions of these various maxima are shown in Table II.

The last row of the table, and the top right hand curve of Fig. 4 (No. 6), show the data for a run where the scattering was due to elastic

[6] *Note added to proof.* A correction must be applied to all the curves shown in Fig. 4, because of the fact that the small volume, in which the collisions considered take place, varies with the angle of scattering. The radius vectors must be multiplied by sin Θ, and consequently the curves shown in the letter to Nature represent the true scattering per unit solid angle. Table II, showing the positions of the maxima, has had this correction included.

impact. The points are somewhat scattered owing to the difficulty of finding the top of an exceedingly sharp peak in the velocity distribution curve.

The scattering is of completely different character from that due to inelastic impacts. The principal maximum lies further out and is not

TABLE II

Positions of maxima in the angular scattering of electrons of various initial velocities V_i which have lost 20.5 volts energy.[6]

V_i	Positions of maxima		
48.9	24°	—	45° ? 70°
72.3	8	—	
97.5	5	—	50°
195.	<2.5	30°	59
294.	<2.5	30°	69
400.	<2.5	30°	70
400.	7	—	62

so intense relative to the rest of the curve. The fixed peak at 30° does not appear.

Any discussion of these results on the basis of the old quantum theory must inevitably lead to the same difficulties as appear in the explanation of the work of Davisson and Kunsman,[1] on the scattering of electrons in metal films. However Elsasser[7] has shown that this class of phenomenon may be treated as a diffraction effect of the phase waves of De Broglie. More recently Born,[8] on the basis of the Schrödinger wave mechanics, has shown that inelastic collisions should give rise to a periodic variation of scattering with angle, similar to a diffraction pattern. The theoretical side of the problem is however not yet sufficiently advanced to give detailed information on the phenomena to be expected, so that the results above reported cannot be said to substantiate the wave mechanics except in the most general way.

In conclusion I must express my deepest gratitude to Professor Karl T. Compton for extending to me the privilege of working in the Palmer Laboratory and for his constant interest and help, and also to the International Education Board for their support during my stay in Princeton.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
November, 1926.*

* Received December 24, 1926.

[7] Elsasser, Die Naturwissenschaften **13**, 711 (1925).

[8] Born, Zeits. für Physik, **38**, 803 (1926).

IONIZATION AND RESONANCE POTENTIALS IN GALLIUM AND INDIUM

By Charles W. Jarvis

Abstract

The critical potentials of gallium and indium have been experimentally determined by the method of inelastic impact. A simple three-electrode tube and the Hertz-differential tube as a simple three-electrode tube or as a four-electrode tube were used. Ionization was detected by the modified space charge method, by the Lenard method, and by the change in the gap resistance. The following critical potentials below ionization were observed: in gallium vapor 3.07 v. $(2p_2-2s)$, 4.22 v. $(2p_2-3d_2)$, 2.70 v. $(2p_1-2s)$, 3.8 v. $(2p_1-3d)$; in indium vapor 0.30 v. $(2p_2-2p_1)$, 3.03 v. $(2p_2-2s)$, 4.07 v. $(2p_2-3d_2)$, 2.8 v. $(2p_1-2s)$. Two ionization potentials were observed: in gallium vapor 5.8 and 13.2 v.; in indium vapor 6.3 and 14.1 v. The ionization potentials are judged to be accurate to 0.5 volts.

Introduction

THE importance of the exchange of energy between a colliding electron and atom or molecule and the relation of the energy exchanged in spectral excitation is well recognized. The results obtained by the method of electronic excitation have been analyzed with success on the basis of the quantum theory. Thus critical potentials are extremely valuable in establishing the orbital levels of the valence electron. The validity of the theory is further established by the stepwise excitation of lines or groups of lines of the arc series. The excitation of the single line 2537A in mercury at 4.9 volts is an outstanding example. Rather recently it has been recognized that an exchange of energy between a colliding electron and an atom or molecule may not be followed by a spectral process.[1] This exchange is not restricted by the selection principle whereas the absorption and emission of radiation is thus restricted. The interpretation of a critical potential for which there is no certain and definite emission or absorption line is as yet somewhat in doubt. Some of the critical potentials in mercury vapor reported by Franck and Einsporn[2] are in this category.

The present work was undertaken for the purpose (1) of getting an independent check on the work of Franck and Einsporn with mercury; (2) of determining the principal critical potentials in gallium and indium which have not been previously investigated by the method of

[1] Sommerfeld, Atomic Structure and Spectrum Lines, (Trans. by Brose) 3rd Ed.' Ch. 6, 3, pp. 347.

[2] Franck and Einsporn, Zeits. f. Physik **2**, pp. 18–19 (1920).

[3] Mohler and Ruark, J. Op. Soc. Am. **7**, pp. 819–830 (1923).

electronic impact. Mohler and Ruark[3] have made some measurements with thallium of this group. They report that the potential corresponding to the transition $2p_2-2p_1$ masks all other higher resonance potentials.

Apparatus and Method

Three electrode tube. Preliminary work with mercury and most of the work with gallium and indium was done with this type of tube either in its simple form or as a modification of the Hertz differential tube by making proper electrical connections. Fig. 1 represents the three-electrode tube if we consider only these essential elements: filament F_2, cylindrical grid A, and cylindrical plate B. The filament was platinum, oxide-coated. Electrons were accelerated through a relatively large distance to the cylindrical grid A by a potential V_A and were then retarded through a relatively short distance to a cylindrical electrode B by a retarding potential V_B. Galvanometers G_2 and G_1 were inserted to determine the partial current to B and the total current to A. The electrodes were constructed of nickel. In some of these tubes seals were made with De Khotinsky cement, and in others the seals were made by sealing tungsten wire directly into Pyrex glass. The method of applying the potentials to the electrodes was essentially that shown in Fig. 1 for the Hertz differential tube.

High vacua were produced with all types of tubes by means of a Jones' mercury vapor pump backed by a simple mercury vapor pump, in turn backed by a motor driven rotary oil pump. A mercury gauge was inserted between the Jones' high vacuum pump and the tube under investigation. A tube once baked and highly exhausted could be sealed by means of a trap gauge and communication subsequently established with the high vacuum pump while it was in operation at its highest efficiency. Except in case of accidental breakdown, air was never readmitted to the tube after initial exhaustion and baking. A liquid air trap was inserted between the gauge and tube in the case of gallium and indium.

The Hertz differential tube. (a) *Electrodes and filaments.* Fig. 1 shows the electrode arrangement together with the potentiometer scheme used in applying the potentials. An oxide-coated platinum filament F_1 was used as a source of electrons. This was placed very close to the gauze enclosing one end of the inner cylindrical box A. Electrons were accelerated into the box under various potentials, V_A. The electrons diffused out through the side of box A to the cylinder B (1) under zero retarding potential, (2) under a small retarding potential, V_B, usually 0.1 volt. A shielding electrode C was maintained at earth potential in order to reduce the effect of external stray potentials. The filament F_2 was used to determine ionization potentials by the

method of modified space charge. It was sometimes used as the source of electrons when the tube was used as a simple three-electrode tube. It was used as a collecting electrode for positive ions when the tube was used to detect ionization by the Lenard method. Its area would intercept little radiation, and therefore, the results should be little affected by the photoelectric effect.

The electrodes were all made of nickel, B and C from thin nickel sheet and A from nickel gauze of 100 or 150 mesh to the inch. The nickel electrodes were electrically welded to tungsten wires which were sealed directly into the Pyrex tube. The entire tube could be enclosed in a furnace for baking.

(b) *Detection of currents.* The galvanometer G_4 (Fig. 1) was used to determine the constancy of the potentiometer current and also for the

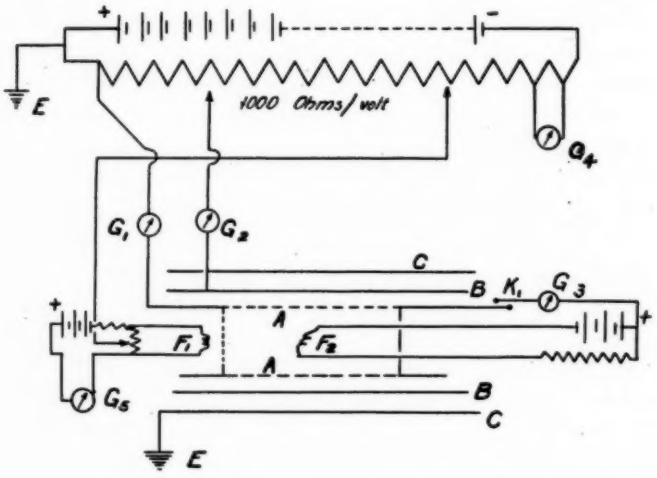

Fig. 1. Arrangement of filaments and electrodes and potentiometer scheme for applying potentials.

detection of ionization by the method of change in gap resistance. A reflecting galvanometer G_5 was inserted in the filament (F_1) circuit and a scale was arranged to receive a spot of light reflected from the mirror of this galvanometer. The scale was so placed as to be under the direct observation of the reader while data were being taken for resonance potentials. The current for F_1 was supplied by two high capacity batteries in parallel and was constant to 1 part in 2000 for several hours. This current was usually of the order of 1.5 amps. The currents as registered by galvanometers G_1 and G_2 were not accepted as trustworthy if there were any indication of a simultaneous change in the galvanometer G_5. Many runs of 10 hours duration were obtained when the filament current was extremely steady and the temperature

of the tube constant to within 1° or 2°C. A moderately sensitive Thomson galvanometer G_1 was used to determine the total current from F_1 to box A, while the partial current from A to B was determined by means of a highly sensitive Broca galvanometer. These galvanometers were also used with the simple three-electrode tubes.

(c) *Method used for resonance data.* For a given value of V_A (the accelerating potential) the galvanometers G_1 and G_2 were read, (1) with V_B equal to zero volts (2) with V_B equal to 0.1 volts. The reading of G_2 with V_B equal to zero volts we call R_1 and the reading with V_B equal to 0.1 volt we call R_2. Then $R_1 - R_2$ gives the value of the differential current corresponding to the potential V_A. Thus one point on the differential current-voltage curve is obtained. In most of the work the voltage V_A was increased in steps of 0.1 or 0.2 volts. In this way the data for the resonance curve as shown in Fig. 2*D* was obtained. In case it was desired to plot the total current curve the reading of galvanometer G_1 was used.

(d) *Method used for ionization data.* The data for the ionization curves shown in Figs. 2*A* and 2*D*, and 3*F* were obtained by the method of modified space charge. To obtain these curves the values of V_A were plotted against the current obtained from the readings of the galvanometer G_3 (Fig. 1). The connections were altered to obtain these data. The connection between G_2 and B was broken, B and A being connected externally, and the key K_1 closed to insert the galvanometer G_3 into the circuit between F_2 and A. Consideration of Fig. 1 will show that the filament F_2 is negative with respect to A. Consequently, electrons would be accelerated toward A and the current registered by G_3 and limited by space charge would remain constant for a constant current through F_2 and for all values of V_A below the ionization potential. This constancy is shown by the flat portions of the ionization curves. When V_A is made large enough that the electrons entering box A have sufficient energy to ionize, then a neutralization of part of the negative space charge in A takes place with the consequence of a sudden rise in the current as registered by the galvanometer G_3. This sudden rise is interpreted as the ionization point. Of course the value of V_A at which this takes place needs correction.

In the Lenard method filament F_2 was maintained negative with respect to all other electrodes and the galvanometer G_2 was connected to it, the battery and galvanometer G_3 being disconnected from F_2. In this method the initial rise in current to F_2 as registered by G_2 so connected was interpreted as the ionization point. (See Fig. 3, curve *G*, for indium.)

At the ionization point there is a change in the gap resistance between filament F_1 and the electrode A. Since this is a shunt on a part

of the potentiometer circuit, the current as registered by the galvanometer G_4 increases since the total resistance in series with the potentiometer battery has decreased. This increase in G_4 was found to be coincident with the sudden increase in G_3 due to the modification of the negative space charge in box *A* for mercury. Hence, considerable importance has been given to the modification of the gap resistance for the case of gallium and indium in which the other methods of determining the ionization potentials did not give as definite results as had been hoped for.

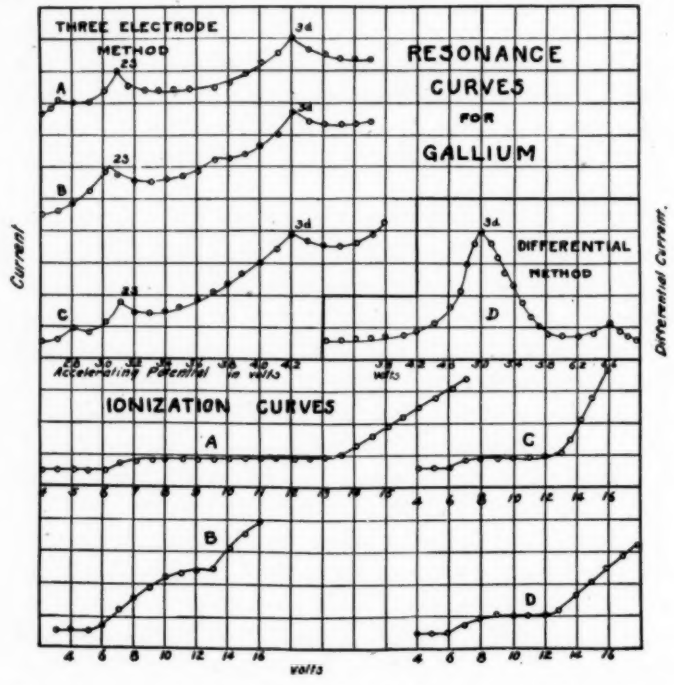

Fig. 2. Curves showing the principal critical potentials for gallium.

(*e*) *Criterion for properly baked tube.* When first exhausted the tubes did not show smooth current potential curves. Baking and pumping was continued until smooth electronic curves were obtained. The vapor to be studied was then admitted and resonance and ionization data secured.

Results

(a) *Mercury.* (*Hertz-differential method.*) The results with this element were reported at the Washington meeting of the American Physical Society (1926), and are given in tabular form in an abstract in the Physical Review.[4] The results are in general agreement with

[4] Jarvis, Phys. Rev. **27**, pp. 808 (June 1926).

those of Franck and Einsporn, with the addition of several values below 4.68 volts. Work is being continued to determine, if possible, the meaning of the critical potentials found below 4.68 volts. Six such critical potentials have been found. It is thought they may be ascribed to the mercury molecule.

(b) *Gallium.* Typical results for gallium are shown in the various curves given in Fig. 2. Both the gallium and indium used were certified as 98.5 percent pure. Two different tubes were used with this element. Three resonance curves shown in the upper left hand portion of the figure were obtained from the Hertz differential type tube used as a simple three-electrode tube. They show transitions corresponding to the $2s$ and $3d$ levels very decidedly. The other resonance curve was obtained with the other tube used in the differential manner. It shows the transition to the $3d$ level as a pronounced peak. This curve gave but slight indication of the $2s$ level.

The results obtained for ionization are shown by the curves A, B, C, and D in the lower portion of Fig. 2. Curves A and D were obtained by the Lenard method, and B and C were obtained by the modified space charge method. Another curve not shown gave marked evidence of ionization at about 6 volts by the method of change in gap resistance. The curves shown have been corrected for filament drop and velocity distribution by an approximate method. These curves give evidence of a weak type ionization at about 6 volts and a stronger second type ionization at about 13 volts. No evidence was obtained indicating the transition $2p_2-2p_1$.

The results for gallium are summarized in Table I. One critical potential at 1.96 volts was found for which there is no corresponding spectral relation. No interpretation is offered for it.

TABLE I

Critical potentials in gallium.

No.	Critical potentials (volts) from different curves					Mean	Calc.	λ	Series
1	2.20	1.80	1.85	2.10	1.85	1.96		6300	?
2	2.70	2.70	2.60	2.80		2.70	2.96	4172*	$2p_1-2s$
3	3.10	3.00	3.00	3.05	3.15	3.07	3.06	4033*	$2p_2-2s$
4	4.20	4.20	4.52	4.25	4.25	4.22	4.29	2872	$2p_2-3d_2$

	Ionization potentials (volts) from different curves.								Mean	Calc
Type 1	5.5	5.8	5.5	6.3	6.0	5.8	6.4	5.5	5.80	5.97
Type 2**	13.0	13.8	12.5	12.8	13.0	13.6	14.0	13.2	13.2	

*4172A and 4033A are "raies ultimes."

** New arc type of ionization.

(c) *Indium.* The various critical potentials found for indium are represented in the curves of Fig. 3. The intermediate portions of the

resonance curves A and B are omitted to facilitate plotting. The latter portions of these curves showing the $3d$ level have had the ordinates reduced in order to keep within the allotted space. Curve A was obtained with a slightly higher filament temperature than curve B and hence the correction is slightly different. Curves A, B, C, and D show critical potentials corresponding to transitions to the $2s$ and the $3d$ levels for indium as decided peaks. The retarding potential applied between electrodes A and B (Fig. 1) was kept constant at 2.5 volts

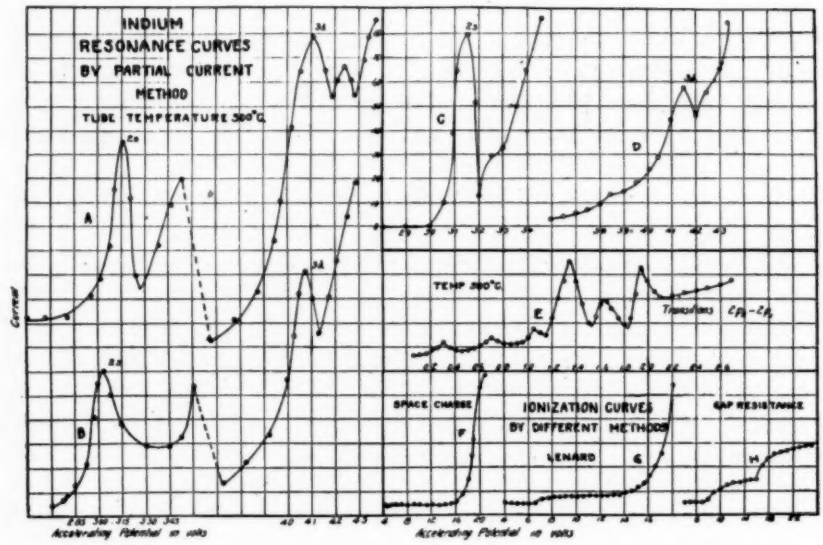

Fig. 3. Curves showing the principal critical potentials for indium.

while data were being taken for curves A, B, C, and D. The filament F_1 was shielded with a nickel shield, only the hottest portion being exposed to box A. Only a slight correction was necessary. The tube was equivalent to a four-electrode tube in which the two inner grids were at the same potential. Some of the curves show a double peak, the separation being 0.1 to 0.2 volts. This may be due to the transition $2p_2-2p_1$ of either gallium or indium. Curve E was obtained with a small retarding potential in order to bring out the transition $2p_2-2p_1$ whose theoretical value is 0.273 volts. The analysis of eight such curves is given in the upper portion of Table II. These results are obtained as differences between recurring peaks on the same curve. The results on ionization are shown by the three curves F, G, and H obtained by the modified space charge, the Lenard, and the gap resistance methods, respectively. Two types of ionization at 6 and 14 volts, approximately, are evident from these curves.

Discussion of Results

(a) *Gallium and indium.* The curves give no evidence of the transition $2p_2-2p_1$ for gallium unless an occasional double peak with 0.1 to 0.2 volt separation could be so interpreted. Spectral considerations place these levels 0.102 volts apart, and it may be that they are too close together to be clearly distinguished by the method of inelastic impact. Foote and Mohler[5] have found a series of recurring peaks at

TABLE II

Critical potentials in indium.

Transition	Curve No.	Potential (volts) of peaks						Mean diff.
$2p_2-2p_1$	1	0.55	0.85	1.15	1.47	1.75	2.04	0.30
	2	.30	.70	1.06	1.35	1.65	1.93	.32
	3		.77	1.07		1.56	1.85	.26
	4		.60	.89	1.17			.28
	5		.60	.94	1.25	1.55		.32
	6	.34	.65	1.05	1.32	1.62		.32
	7		.65	.95	1.25	1.55		.30
	8	.30	.56	.88	1.15	1.40		.28
						Mean of means		0.297
						Calculated value		.273

Transition	Volt values from different curves							Mean	Calc.
$2p_2-2s$	3.05	2.96	3.00	3.01	3.05	3.15	2.96	3.03	3.01*
$2p_1-3d$	4.05	4.00	4.20	4.05	4.06	4.12	3.97	4.07	4.06**

Ionization	Potentials of breaks				Mean (corr.)	Calc.
Type 1	7.5	8.5	6.7	7.0	6.3±0.5	5.76
Type 2***	15.2	15.4	15.0	14.8	14.1±0.5	

* Corresponding absorption line 4102A.
** Corresponding absorption line 3039A.
*** New arc type of ionization.

0.9 volt apart for thallium agreeing well with the series relation for the $2p_2-2p_1$ transition. The author's value of 0.297 volt is in fair agreement with 0.273 volts based on series relations for the transition $2p_2-2p_1$ in the case of indium. All curves for gallium show the transitions $2p_2-2s$ and $2p_2-3d_2$ and several (see curves *A* and *C* for resonance, Fig. 2) show the transition $2p_1-2s$. Grotrian[6] and Frayne and Smith[7] have shown that for gallium and indium the lines of the series $2p_1-ms$ are absorption lines as well as those of the series $2p_2-ms$. This work is in agreement with theirs but would indicate that the transition $2p_2-ms$ is

[5] Foote and Mohler, Phil. Mag. **37**, pp. 35–50 (1919); also J.O.S.A. **7**, pp. 819–830 (1923).

[6] Grotrian, Zeits. f. Physik **18**, pp. 169–192 (1923); also **12**, pp. 218–231 (1922).

[7] Frayne and Smith, Phys. Rev. **27**, p. 23 (1926).

more probable than the transition $2p_1-ms$. Several curves for gallium (see curve *B*, Fig. 2) gave evidence of a critical potential at approximately 3.8 volts which corresponds to a wave-length of 3260A. This line is the first member of the series $2p_1-md$ and was found as an absorption line by Grotrian[6] and also by Frayne and Smith.[7] With indium the transitions corresponding to the levels $2s$ and $3d$ came out consistently as well as the transition $2p_2-2p_1$. However, a few curves (not shown in Fig. 3) gave pronounced evidence of the transition $2p_1-2s$ and $2p_1-3d$. The results with both gallium and indium are in fair agreement with the spectral series arrangement. One value for gallium at 1.96 volts has not been reconciled with spectral data. With both gallium and indium the second type of ionization at 12 to 14 volts was found to give the more pronounced breaks in the potential curves. It is thought that the second valence electron is involved at this point. If this be true, then additional spectrum lines should appear at this voltage. Spectroscopic investigation of this point has been undertaken by Frayne and Jarvis[8] for indium. Their results will appear in a later issue of the PHYSICAL REVIEW.

In conclusion the author expresses his gratitude to the Physics Department of Ohio State University where this work was done, and to Dr. Alpheus W. Smith under whose direction and sustaining influence this work was carried out.

OHIO WESLEYAN UNIVERSITY,
September 1, 1926.

[8] Frayne and Jarvis, PHYS. REV., in press.

THE PHOTOELECTRIC PROPERTIES OF THOROUGHLY OUTGASSED PLATINUM[1]

By Lee A. DuBridge

Abstract

Effect of heat treatment on the photo-currents from Pt.—The total photoelectric emission from a strip of Pt foil excited by the full radiation from a quartz mercury arc was studied while the strip was put through an extended heat treatment in pressures as low as 10^{-8} mm Hg as read on an ionization gauge. Prolonged heating at 1200°–1400°C caused the photo-current to decrease to a final value which could not be further reduced by additional heating for as long as 300 hours at temperatures up to the melting point. The photo-current was found to increase spontaneously from the low values observed immediately after a heating interval to much higher values if the strip was allowed to remain at room temperature for a short time. After thorough outgassing of the strip and the tube however this "recovery" effect finally disappeared.

Effect of heat treatment on the long wave-length limit of Pt.—The long wave-length limit was determined by using filters of dilute acetic acid in a fluorite cell to cut out the shorter Hg lines. The threshold was found to shift during outgassing from above 2500A to a final steady value of 1958 ± 15A. This is at variance with Suhrmann's value of 2675A but is shown to be in agreement with the work of Tucker and Woodruff. Pressure readings taken with an ionization gauge of high sensitivity confirm the conclusions (a) that decreasing photo-currents are caused by the evolution of absorbed gases, (b) that increasing photo-currents (recovery effect) are due to the adsorption of gas by the cool Pt surface, and (c) that the final low values of the photo-emission are characteristic of the gas-free Pt. Heating an outgassed strip in air at 0.015 mm pressure caused the photo-currents to disappear; heating in hydrogen at the same pressure caused them to increase. They were brought back to values characteristic of the completely outgassed state in each case by heating for 30 sec. at a pressure of 10^{-4} mm.

Influence of temperature on the photo-emission from Pt.—The photoelectric effect of Pt is found to be independent of the temperature only in the region below 500°C. At higher temperatures up to 1200°C the photo-currents increase considerably with temperature and the threshold shifts slightly to the red. Several explanations of the effect were tested and are discussed, the conclusion being that it is a genuine temperature effect characteristic of the metal itself and due to the increase in the thermal energies of the "free" electrons which may become appreciable at the higher temperatures.

Introduction

IN SPITE of the large amount of recent research on the subject, the status of the problem of the photoelectric behavior of metals which have been thoroughly cleaned of occluded gases is still a rather un-

[1] A preliminary report of this work appeared in Proc. Nat. Acad. Sci. **12**, 162 (1926).

certain one. Strange to say, however, the principal points of disagreement between various observers lie not so much in the experimental facts observed as in the conclusions drawn from them and in the explanations offered. In the case of platinum, for example, while there is general agreement as to the type of behavior observed when the photo-current excited by the radiation from a quartz mercury arc is studied as a function of the time for which the specimen has been outgassed by heating, there are still three questions at least upon which the experimenters in this field are divided, namely: (1) the old problem of whether the observed decrease in the photo-current with outgassing continues indefinitely, or whether it is possible to reach a limiting state characteristic of the cleaned metal itself; (2) the question as to which, if any, of the many observed values of the photoelectric threshold may be accepted as the true value characteristic of the platinum; (3) the problem of formulating a theory to explain the effects of gases and to account for the observed results. The experimental work to be described in the present paper was undertaken for the purpose of obtaining further evidence on all three of these questions. Reviews of previous work in this field have been given by other writers[2] and only a brief statement of the present status of each problem will be given here.

In regard to the first, Wiedmann and Hallwachs[2] and their students have been led to the view that the photoelectric effect is not an intrinsic property of the metal at all but that, as outgassing progressed, the photo-currents excited by the light ordinarily used would disappear, and the long wave-length limit would shift steadily further into the ultra-violet, reaching finally the region near 1200A where ionization of the gas atoms themselves begins. Other observers[3,4,5] are inclined to the view that the platinum itself is the seat of the photo-currents and that the absorbed gases merely assist (or hinder) their escape; that it should be possible to reach a state where the photo-currents from the Pt itself are obtained and where the threshold, while it may be far in the ultra-violet, still has a value characteristic of the cleaned metal, unaffected by the presence of gases. Actually to reach such a state has proved to be a difficult task.

The second problem, that of the characteristic long wave-limit of Pt, is thus seen to be intimately connected with the first. Observed values of the threshold have been pushed steadily to shorter wave-lengths as more complete outgassing has been attained, and Tucker[6] and

[2] See Wiedmann, Jahrb. d. Radioakt. u. Elekt. **19**, 112 (1922). See also refs. 5, 6, 9.
[3] Welo, Phys. Rev. **12**, 251 (1918); Phil. Mag. **45**, 593 (1923).
[4] Piersol, Phys. Rev. **8**, 238 (1916).
[5] Woodruff, Phys. Rev. **26**, 655 (1925).
[6] Tucker, Phys. Rev. **22**, 574 (1923).

Woodruff[5] have reported specimens which were insensitive to the mercury arc radiation for a short time after long heating. Tucker concludes that this indicates a threshold below 1850A though Woodruff believes it may be as high as 2200A because of the observed weakness of the shorter lines in the spectrum. Suhrmann[7] on the other hand reports a limiting value of 2675A after long heating. Obviously before acceptable final values of the threshold can be obtained, a stable limiting state of the specimen must be reached in which the photo-currents remain unchanged during further intense treatment. This condition has not heretofore been realized in the case of Pt, though Kazda[8] seems to have attained an analogous condition in the case of flowing mercury.

The third problem—that of formulating a theory to account for the effects of gases—has also presented difficulties. The theory which has been most widely accepted as explaining the largest number of observed facts is that of Wiedmann and Hallwachs[9] who assumed, (a) that the initial low sensitivity observed for a fresh platinum specimen is due to the presence on the surface of an adsorbed layer of electro-negative gases which tends to prevent the escape of electrons, this surface layer being quickly removed by the heat treatment giving rise to a large initial increase in the photo-current; (b) that in addition there are gases absorbed within the body of the metal itself which in some way aid in the ejection of electrons, and their gradual removal during heating causes the photo-current to decrease slowly and the threshold to shift into the violet. The implied consequence of this theory was that if all absorbed gases could be removed the photo-currents would disappear.

These assumptions have been confirmed in many respects by the experimental work of Sende and Simon,[10] Suhrmann,[11] and Herrmann,[12] but Welo,[3] Piersol[4] and Woodruff[5] have been led to the conclusion that they do not account for many observed facts. The latter observers regard the Pt as the seat of the photo-electrons and believe that occluded gases retard rather than assist in their emission. An attempt was made in the present work to obtain a more direct test between these viewpoints.

METHOD

Several experimental tubes of slightly different forms were used, a diagram of one of the later ones being shown in Fig. 1. The specimen

[7] Suhrmann, Zeits. f. Physik **33**, 63 (1925).
[8] Kazda, Phys. Rev. **26**, 643 (1925).
[9] Wiedmann and Hallwachs, Verh. d. Deutsch. Phys. Ges. **16**, 107 (1914).
[10] Sende and Simon, Ann. d. Physik **65**, 697 (1921).
[11] Suhrmann, Ann. d. Physik **67**, 43 (1922); Zeits. f. Physik **13**, 17 (1923).
[12] Herrmann, Ann. d. Physik **77**, 503 (1925).

to be tested consisted in a strip of Pt foil, .01 mm thick, 2 mm wide and about 10 cm long, hung in the form of a loop inside the receiving cylinder *C* of nickel or molybdenum. The strip could be heated by a current from a 20 volt storage battery conducted in through the tungsten leads *T* to which the strip was spot-welded. Its temperature could be measured by means of an optical pyrometer focussed onto it through the thin window *W*. The true temperature was determined

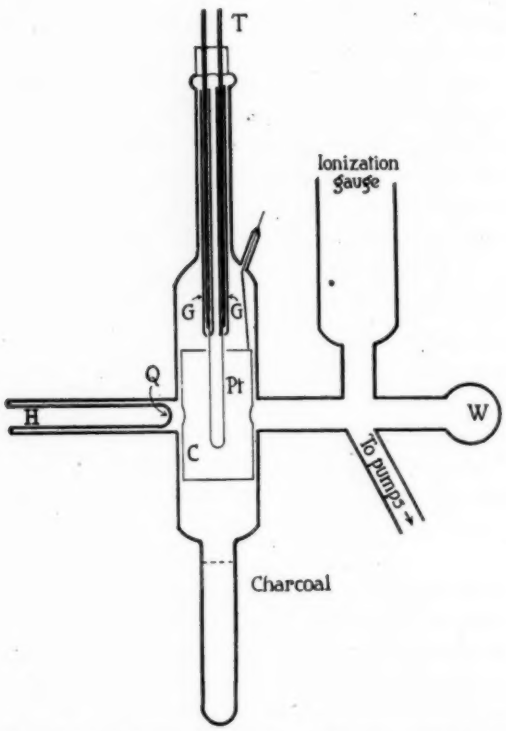

Fig. 1. Photo-electric tube. *Q*, quartz window; *W*, pyrometer window; *c*, collecting cylinder; *GG*, Pyrex tubes to shield tungsten leads, *T*.

from the observed black body temperature using data published by Mendenhall.[13] Light from a Cooper-Hewitt Type Y, 110 volt quartz mercury arc, or from a metallic spark, could be focussed by means of a quartz lens through the quartz window *Q* onto the Pt. The window *Q* was sealed to the pyrex tube without the use of wax or cement by a graded quartz to pyrex seal. Since nearly all the runs were carried out at pressures below the range of measurement of the McLeod gauge these lower pressures were measured by a sensitive ionization gauge of the type described by Dushman and Found.[14] The apparatus was

[13] Mendenhall, J. Astroph. **33**, 91 (1911).
[14] Dushman and Found, Phys. Rev. **23**, 734 (1924).

connected to the pumps without the use of wax or cement joints to avoid troubles arising from their use. Outgassing at 550°C was possible.

The photo-currents were measured by a Compton electrometer whose sensitivity was 5000 mm per volt. A resistance of 400 megohms shunted across the quadrants permitted the currents to be measured by the "steady deflection" method, the current sensitivity being 5×10^{-13} amp/mm.

In order to prevent scattered light from striking the tungsten supports *T*, or the upper parts of the strip which were not thoroughly outgassed, these were kept well above the top of the cylinder and were enclosed in small pyrex tubes *GG* which prevented light of shorter wave-lengths from reaching them and also prevented any electrons leaving them from reaching the cylinder. All of the observed currents then came from the lower parts of the strip which were heated to a uniform temperature.

To furnish to the strip if necessary more energy in the shorter wave-lengths, the region *H* could be converted into a hydrogen discharge tube by an obvious device. The hydrogen discharge is known to be rich in wave-lengths between 2200A and 1600A.

After an initial cleaning of the Pt, the entire apparatus was baked out at temperatures up to 550°C for periods varying from several hours to several days—or until the pressure with the tube hot had been reduced to 10^{-6} mm Hg or less. In some cases the Pt strip was glowed at a dull red heat during baking. After this treatment the photo-current was quite large, its actual value depending upon the time for which the treatment had been continued in each particular case. The Pt strip was then heated by an electric current for various intervals of time and at various temperatures, photo-current readings being taken intermittently during the process. The heating current through the strip was shut off while the photo-current was being measured. During the heating at higher temperatures the cylinder *C* could be rotated about a vertical axis by means of an external magnet to bring the holes in the cylinder out of line with the windows *Q* and *W* to prevent condensation of platinum on these windows.

The Total Photoelectric Current

Photo-current readings using the mercury arc as a source were taken on 15 different specimens of Pt, cut from foil obtained from three different sources, all of high purity. The strips were subjected to a variety of cleaning treatments before being introduced into the tube, and to many different forms of heat treatment after being sealed in. All, however, exhibited substantially the same form of final behavior of the total photo-current as a function of the time of heating, viz., in every case in which the heating was carried on for a sufficient length

of time the photo-current eventually reached a final limiting value, —not zero—which value could not be further reduced by heating of any kind.

Observations on three typical specimens have already been published[1] and those for a fourth are presented herewith (Fig. 2). This curve may be taken as typical of all the runs which were taken. The maxima in the curve at 22 hours and 50 hours of heating are characteristic of the irregularities which often appeared in the first part of the curves and seemed to be due to incidental pressure variations which were unavoidable during the initial stages of outgassing. Many of the curves

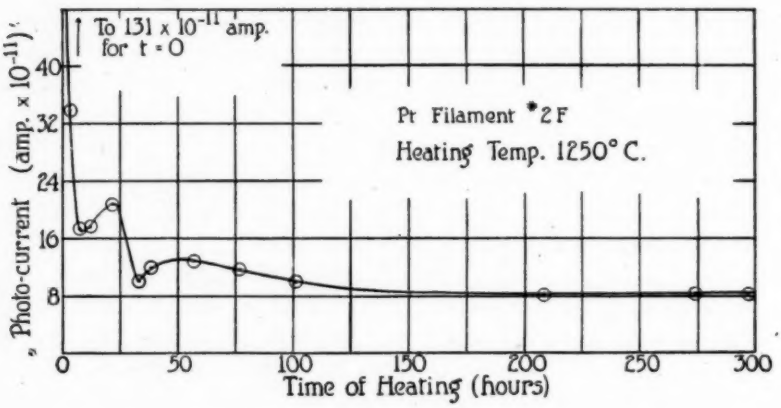

Fig. 2. Variations in the total photo-current during outgassing.

showed no irregularities at all, but in any case they all gradually disappeared as the heat treatment progressed, so that the photo-current approached a limiting value which was truly a stable one.

It should be emphasized that this limiting value is reached only after the heating has been carried on for long periods of time at temperatures higher than 1100°C and at pressures lower than 10^{-6} mm. While the actual number of hours of heating required varied considerably with the temperature and the pressure conditions, in no case was a true final value of the photo-current attained, even at the highest heating temperatures, in less than 10 hours of actual heating time. In most cases at moderate temperatures (1200°–1400°C) from 20 to 50 hours were required, while in some cases, as in Fig. 2, the limiting value was reached only after 150 hours of heating. Furthermore, the value of the photo-current observed in the final outgassed state was the *same* for *all* Pt specimens which were studied under the same set of incident light conditions.

Every effort was made to determine whether this final value of the photo-current could not be reduced by some type of further treatment.

Among the procedures which were tried were the following: (a) heating for still longer intervals of time at the higher temperatures, up to 1500°C; (b) "flashing" intermittently for intervals of a few seconds each at still higher temperatures, close to the fusion point (a procedure suggested as the most effective one by Herrmann[12]); (c) heating for long periods at temperatures at which considerable vaporization of the Pt took place, thus cleaning off the outer surface of the specimen; (d) heating in the immediate presence of a mass of charcoal cooled by liquid air the more rapidly to absorb the evolved gases; (e) heating the strip while the entire tube around it was lowered to liquid air temperatures by means of a copper jacket; (f) further reducing the pressures to as low as 10^{-8} mm by additional baking out and heating of all metal parts at the highest possible temperatures. All these methods were, however, equally ineffective in lowering the final value of the photo-current, though most of them when tried on a fresh specimen did cause it to reach its limiting value more quickly. A thoroughly cleaned specimen is thus still sensitive to the arc radiation.

A phenomenon reported by Woodruff and by Tucker and referred to as the "recovery" of the photo-emission was also studied in this connection. When the Pt strip is allowed to stand at room temperature for a short time immediately after a heating interval, the photo-current increases spontaneously up to a value which depends upon the previous heat treatment and the pressure and which may be only a few percent less than the maximum value observed during the initial stages of outgassing. It was found by the author, however, that this recovery becomes less rapid and the final value reached becomes steadily smaller as the outgassing progresses and the pressures in the tube become smaller. If the outgassing is carried on long enough that the pressures are reduced to below 10^{-7} mm the effect finally disappears entirely and the photo-currents observed immediately after heating remain constant for many hours. This phenomenon will be more fully discussed later in connection with the pressure effects which were found to accompany it. (See Fig. 3.)

The Long Wave-Length Limit

The variations of the long wave-length limit of Pt described in the previous paper[1] have been checked on other specimens, using as before light filters to cut out successively the shorter lines in the mercury spectrum,—a method used by Williamson.[15] These experiments quite definitely place the photoelectric threshold for Pt cleaned by the process already described in the region between the mercury lines λ1943 and λ1973.

The filters used in these determinations consisted of weak solutions of acetic acid in distilled water, introduced into an absorption cell with

[15] Williamson, Phys. Rev. **21**, 107 (1923).

fluorite windows which was placed in the path of the incident light. The thickness of the fluid layer in the cell was 3.2 cm. Photographs taken with a Bausch and Lomb quartz spectrograph, using Schumann plates,[16] showed that in the light transmitted by the empty cell the shorter mercury lines including λ1850 were present with considerable strength. Distilled water in the cell served to cut out the 1850 line alone, leaving λ1943 still quite strong. A solution formed by adding three drops of 36 percent acetic acid to 25 cc of water when placed in the cell cut out the 1943 line and all below, leaving 1973 still quite strong. Adding six drops of acetic acid to 25 cc of water gave a solution which cut out λ1973. The longer wave-length lines were cut out using the solutions described by Williamson.[15]

When a fresh strip of Pt was tested after a long initial baking at about 500°C the photo-current could be reduced to zero only after all lines of the mercury spectrum up to and including λ2482 had been cut out by filters. The threshold for such a specimen is thus in the neighborhood of 2500A. After long outgassing, however, and after the photo-current had reached its limiting value, it could be reduced to zero by the filter which cut out the 1943 line and all below it leaving λ1973. It was not reduced to zero by cutting out λ1850 alone leaving λ1943. The threshold has thus been shifted to the region between 1943 and 1973A. Using an aluminum spark as a source the threshold was similarly found to lie between the Al lines λ1930 and 1990. The photo-current was taken to be "zero" in the above observations only when no observable deflection of the electrometer was obtained even after its sensitivity had been increased up to its maximum value by increasing the potential on the needle. In every case a current as great as .05 percent of that produced by the total arc radiation could be easily observed. These results appear at first sight to be in conflict with those of Tucker[6] and Woodruff,[5] but there is a possibility, suggested by Woodruff, that in their work the radiation below about 2200A was too weak to be effective.

If we assume the photoelectric threshold for thoroughly outgassed Pt to be in the neighborhood of 1958A and make use of the quantum relation

$$h\nu_0 = \phi e,$$

we may calculate the work function ϕ for such a surface. The value so obtained is 6.3 volts. The commonly accepted value for the thermionic work function of Pt is 5 volts though this is probably not the value for a thoroughly outgassed surface. Langmuir[17] reports a value

[16] The author is indebted to Mr. H. R. Lillie of this laboratory who made up the numerous Schumann plates required.

[17] Langmuir, Phys. Rev. **2**, 452 (1913).

of 6.6 volts for a surface which had been subjected to special heat treatment, and Woodruff also found high values for his outgassed surfaces.

Relation between Photoelectric Currents and Surface Gas-Content

In order to obtain more exact information on the observed variations in the photoelectric emission as related to the corresponding changes in the gas-content of the specimen and the gas pressures in the tube, a close record was kept of the ionization gauge readings during the runs on several Pt strips. The first point of interest in connection with these readings was to determine how the amount of gas being given off by the specimen during heating varied as the outgassing progressed. The readings for a typical run are given in Table I. In this table are

TABLE I

Progressive changes in pressure and photo-current during heat treatment.

Time of heating	Temp. °C	Pressure $\times 10^{-7}$mm		Ratio	Photo-curr. $\times 10^{-11}$amp.
		Fil. cold	Fil. hot		Fil. cold
10 min.	1250°	5.2	120.0	23.1	84.0
3 hr.	"	4.0	14.0	3.5	26.0
19 "	"	3.2	7.3	2.3	21.0
39 "	"	2.2	4.0	1.82	12.0
107 "	"	0.8	1.2	1.50	8.6
296 "	"	0.25	0.25	1.00	8.5
320 "	1360°	0.10	0.10	1.00	8.5

recorded the steady pressures as read by the ionization gauge while the Pt strip was glowing and while it was at room temperature, at various stages during the heat treatment. The pumps were running continuously during all readings.

These readings were taken on the same specimen whose photoelectric behavior is recorded in Fig. 2. It is seen at once that initially the filament was so saturated with gas that bringing it to a temperature of 1250°C caused a 23-fold increase in the pressure in the tube. After 296 hours of heating, however, during which time the photo-current had reached its limiting value, there was no change in the pressure when the heating current through the strip was turned on, showing that the evolution of gas from the specimen had practically ceased. After the readings recorded in the table were taken the strip was heated irregularly at various temperatures up, finally, to the fusion point, over a period of several days while temperature variation runs were in progress. During this time the pressure and the photo-current remained practically unchanged at the final values given in the table. Evolution of gas from the Pt thus ceases only after extended periods of outgassing—and only after this evolution of gas has ceased are stable

values of the photo-current attained. These observations then confirm the view that occluded gases *assist* rather than hinder the escape of photo-electrons and that their gradual removal causes the photo-currents to decrease.

Further confirmation of this view was found in a more careful study of the "recovery" of the photo-current when the strip was allowed to stand at room temperature for a short time. It was found that after such a period of standing, switching on the heating current through the Pt strip released a large amount of gas from the strip causing an instantaneous increase in the pressure in the tube. In the curves of Fig. 3 the magnitude of this pressure increase is plotted as a function of the time for which the strip had been standing cool. After only 50 hours of outgassing (Curves I and II) if the strip was allowed to stand at room temperature for 10 minutes, turning on the heating cur-

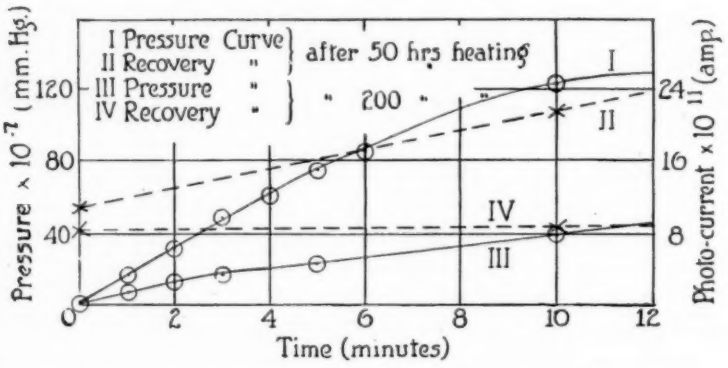

Fig. 3. Recovery of photo-current and accompanying pressure effects.

rent caused a sudden rise in the pressure from 2.0×10^{-7} mm to a peak value of 123×10^{-7} mm. During the same interval the photo-current nearly doubled its initial value. After 200 hours of outgassing (Curves III and IV) the pressure rise due to 10 minutes of standing was only from 1.2 to 40×10^{-7} mm and the rise in photo-current during this interval was only 4 percent. After 300 hours of heating (curves not shown) the rise in pressure as well as the increase in photo-current had practically ceased. The pressure rise caused by heating after a 10 minute interval at room temperature was only from 0.18 to 0.20×10^{-7} mm and after a two hour interval was only to 1.1×10^{-7}. The photo-current during the 10 minute interval now remained constant within the limits of observational error and in the two hour interval increased less than 8 percent.

These results point at once to the conclusion that the recovery of the photo-current is due to the formation on the cool Pt surface of a

gas layer which *increases* the photo-sensitivity of the metal. This layer evaporates at once when the strip is again heated, causing the instantaneous rise in pressure observed. When the Pt strip as well as the rest of the tube have been thoroughly cleaned of occluded gases this surface layer no longer forms and the recovery of the photo-current disappears. The fact that both these effects may be made to reappear by admitting a small amount of air into the tube indicates that the surface layer is formed by deposition on the cool Pt of residual gases in the tube. On the other hand the fact that the formation of the layer ceases only after the strip itself has been thoroughly outgassed might lead to the conclusion that the layer was formed on the surface by diffusion of gases from the interior of the metal. More data are needed to settle this point. In any case the above data on the formation of loosely bound surface layers seem to be in definite disagreement with the view advanced by Woodruff and Welo that the low final values of the photo-current are due to the presence of retarding layers, and in favor of the view that they are characteristic of the outgassed Pt itself. A Pt strip when most completely freed from gases is sensitive only to radiation of wave-length shorter than about 1958A.

If then the *final* low values of the emission are characteristic of the metal itself, the *initial* low values observed before any outgassing is begun must be due to a retarding layer formed on the specimen before it is introduced into the vacuum chamber. It seems probable that this may be a layer of oxide or adsorbed oxygen and nitrogen since it was found that heat ng the outgassed strip for 30 seconds in dry air at a pressure of 0.015 mm actually caused the photo-current to disappear. Heating again in vacuum brought the sensitivity back to the value characteristic of the outgassed metal. On the other hand heating the strip in hydrogen admitted through a palladium tube to a pressure of 0.015 mm caused a large increase in the photo-current, and it was again brought back to normal by short heating in vacuum. The high values of the photo-current which persist even after considerable outgassing are thus probably due to the presence of hydrogen, and possibly water vapor, which are notably hard to remove from the tube and which are readily absorbed by the Pt. Herrmann[12] and Suhrmann[11] have arrived at a similar conclusion, which also is consistent with data obtained by Welo.[18]

Variation of the Photo-Current with Temperature

The temperature variation of the total photoelectric current previously reported[1] has been more carefully studied and its existence more firmly established. At temperatures between 1100°C (at which the thermionic emission is just perceptible) and 1250° (above which

[18] Welo, Phil. Mag. (7) **2**, 463 (1926).

the thermionic emission swamps the photoelectric current) the value of the photo-current was obtained by subtracting the electrometer reading obtained when the light from the arc was cut off from that obtained when the light was focussed on the specimen.

The results show that for thoroughly outgassed Pt the ordinarily assumed independence of the photoelectric effect of the temperature holds quite accurately for temperatues below about 500°C. Increasing the temperature of the specimen above this point however causes the photo-current to rise, slowly at first and then more rapidly, until at 1200° it is practically double its value at room temperature. Three explanations for such an effect may be offered, namely: (1) The variation might be due to the change with rise in temperature of the thickness or density of a surface gas layer; (2) it might be due primarily to the heating current through the strip rather than to the temperature, as suggested by the work of Shenstone[19]; (3) it may be a true temperature effect characteristic of the metal.

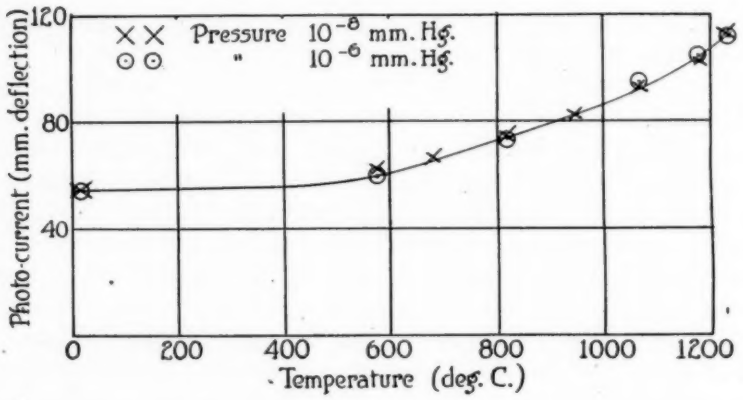

Fig. 4. Temperature variation of the photo-current.

To test the first possibility a large number of runs were taken on several specimens to determine whether the phenomenon exhibited the characteristics which would be expected of a gas effect. The results may be summarized as follows:

(a) The temperature variation described above is characteristic only of the thoroughly outgassed metal. During the earlier stages of outgassing the photo-current showed wide, irregular and non-reproducible changes with temperature, of the type obviously caused by the presence of gas. As the outgassing progressed the behavior gradually became more regular and ultimately settled down to the consistent type of variation shown in Fig. 4.

[19] Shenstone, Phil. Mag. **41**, 916 (1921); **45**, 918 (1923).

(b) When this stage was reached the photo-current—temperature curves taken with temperatures increasing were coincident with those taken with decreasing temperatures,—a result which might not be expected of a phenomenon conditioned by gas-content.

(c) In the thoroughly outgassed state the ionization gauge showed no observable change in pressure in the tube when the temperature of the Pt strip was raised from 20° to 1250°C even when connection with the pumps had been broken by means of a mercury cut-off. The temperature variation thus cannot be due to evolution of gas from the specimen.

(d) The values of the photo-current at the various temperatures were independent of the residual gas pressure in the tube, as long as this was below 10^{-6} mm. In the curve of Fig. 4 the crosses and circles represent points taken with the tube pressure at 10^{-6} and 10^{-5} mm respectively. This result would also not be expected were the photo-currents being affected by the presence of a gas layer, since the characteristics of such a layer should depend upon the surrounding pressure.

It is considered that these results contain sufficient evidence to warrant discarding (1) as a possible explanation of the temperature variation.

That this variation is due primarily to the change in the current through the strip rather than to the temperature seems improbable since the variations of this type reported by Shenstone were very irregular in their nature, showing many time-lag effects when the current was on, and persisting for some time after the current which produced them had been shut off. The variation observed by the author showed none of these effects. Shenstone reported no results for Pt, but it seems evident from the results reported herein that the type of effect which he discovered does not exist for outgassed Pt.

We may then conclude that we are dealing with a true temperature variation of the photoelectric effect. It will be seen from the curve that the type of variation observed is not in disagreement with the results of previous observers who have reported the photoelectric current to be independent of the temperature, since previous observations were carried out in nearly every case at temperatures below about 600°C. It is only at higher temperatures that an appreciable variation is observed.

An increase in the photo-current with rise in temperature might be caused either (a) by an increase in the number of free electrons in the metal made available for ejection by the incident light, (b) by a decrease in the surface work function, or (c) by an increase in the thermal energy of the electrons. In the case of (b) or (c) the increase should be accompanied by a shift in the long-wave limit toward the red while no such shift would occur if the increase were produced by (a) alone.

To determine whether there was such a shift in the threshold, measurements were made of the ratio of the photo-current at 1200°C to that at 20°, *first* using the total radiation of the arc and *second*, when the 1850 line had been cut out by a filter. If these two ratios turned out to be equal this would have been evidence of no shift in the limit. It was found, however, that in the *first* case the ratio was approximately 2 : 1 while in the *second* it was nearly 4 : 1. In other words the change in the photo-current with temperature is greater for the longer wave-lengths (1850 cut out) than for the shorter (1850 included). There has thus been a shift in the threshold toward the red, though it still remained in the region between 1943 and 1973A. Koppius[20] also found evidence for a similar shift in the limit as the temperature was increased from 500° to 700°C. In view of this conclusion (a) must be eliminated as a complete explanation of the temperature variation and we are left to choose between (b) and (c).

Now the work function of a thoroughly cleaned metallic surface is presumably a constant characteristic of the metal itself and is theoretically nearly independent of temperature. Within the (relatively large) limits of error available in thermionic measurements the work function for clean metals is found to be constant over quite wide ranges of temperature. Nearly all the variations in work function (or contact potential) which occur under ordinary conditions can be traced directly to changes in surface contamination,—a factor which it was hoped had been eliminated in these experiments. Moreover any changes in contamination which might be expected to take place with increase in temperature would, in the light of the present results, cause the work function to increase rather than decrease.

We are thus led to conclude that the increase in the photo-current and shift in the threshold toward the red with rise in temperature are due to the increase in the thermal energies of the electrons within the metal. That these thermal energies become appreciable only at the higher temperatures is in line with the postulates of Hall's dual theory of metallic conduction[21] and also with the conclusions to which Millikan and Eyring[22] have been led by their experiments on pulling electrons from metals by intense electric fields. The latter agreement is of interest in its confirmation of the view that the electrons pulled from the metals in these experiments (the "free" or conduction electrons) are the same as those ejected photo-electrically. Moreover if the shift in the threshold is due to the thermal energies of electrons there should be a relation between this shift and the Thomson effect as pointed out

[20] Koppius, Phys. Rev. **18**, 443 (1921).
[21] Hall, Phys. Rev. **28**, 392 (1926).
[22] Millikan and Eyring, Phys. Rev. **27**, 51 (1926).

by Nielsen,[23] and the specific heats of metals at high temperatures, as suggested by the work of Eastman, Williams and Young.[24]

Now in the Einstein photoelectric equation as ordinarily written,

$$Ve = h\nu - h\nu_0$$

Ve represents the maximum energy with which the electrons emerge from the metal, $h\nu$ the energy they receive from the incident light, and $h\nu_0$ is usually assumed to be equal to ϕe, the energy lost by the electron in leaving the surface. Now if the electron through thermal collisions acquires the kinetic energy E_k in addition to the energy received from the incident light, the energy with which it should emerge from the metal is given by

$$Ve = h\nu + E_k - \phi e.$$

On comparison with the previous equation we may now set

$$h\nu_0 = \phi e - E_k,$$

an equation which has also been used by Nielsen.[23] Thus even though the work function ϕ remain constant, ν_0 may alter through a change in E_k in the sense that it will shift slightly to the red at the higher temperatures. As Nielsen has pointed out, the values of E_k will not be the same for all electrons but will be distributed according to Maxwell's law, so that at the higher temperatures the threshold should also show an appreciable lack of sharpness.

Suhrmann[7] has obtained results which he interprets as indicating a shift in the limit toward the red between the absolute zero and room temperature, and also finds an apparent lack of sharpness in the threshold even at room temperature. He attributes both effects to thermal collisions suffered by a few of the electrons even at these lower temperatures. A more detailed study of the variation of the photo-electric threshold with temperature is now being undertaken by the author.

In conclusion the author wishes to express his appreciation to Prof. R. C. Williamson for numerous valuable suggestions and to Mr. A. B. Cardwell for his assistance during the latter part of the experimental work; and especially to acknowledge his very great indebtedness to Prof. C. E. Mendenhall under whose kindly supervision the above work was carried on.

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[23] Nielsen, Phys. Rev. **25**, 30 (1925).
[24] Eastman, Williams and Young, J. Am. Chem. Soc. **46**, 1184 (1924).
* Received October 25, 1926.

THE EXCITATION OF FLUORESCENCE IN FLUORESCEIN

By E. H. Kennard

Abstract

Fluorescence in violation of Stokes' law, excited in an alcoholic solution of specially purified fluorescein, was compared by a photoelectric method with the reciprocal emission when fluorescent and exciting wave-lengths are interchanged. The following theoretical equation, recently proposed by the author, was found to be largely verified: $f_{yx}/f_{xy}=\lambda_x J_y/\lambda_y J_x$. Here f is the exciting power, i.e. $f_{yx}d\lambda_y$ is the emission of fluorescent energy from unit volume in the wave-length range $d\lambda_y$ when the fluorescing substance is illuminated with unit density of exciting radiation of wave-length λ_x, f_{xy} is the same thing with the wave-lengths interchanged, and J_x, J_y are the densities of black-body radiation for these two wave-lengths at the temperature of the fluorescing substance. A peculiar interest attaches to this equation because it contains no unknown constants.

Fluorescence, excitation and absorption curves for the same fluorescein were also determined with moderate accuracy. The fluorescence curves show a single maximum around 5240A but change shape as the exciting wave-length is varied. The excitation curve for fixed incident energy shows a maximum around 5000 for fluorescence at 5270; for other points in the fluorescence spectrum the maximum excitation occurs at shorter wave-lengths, e.g. at 4730 ± 80A for fluorescence at 5009 or 5582. The curves suggest two superposed bands of different width but with almost coincident peaks. The maximum absorption occurs around 4750.

IN a recent paper[1] in the PHYSICAL REVIEW the writer obtained the following theoretical equation concerning the excitation of fluorescence:

$$\frac{f_{yx}}{f_{xy}}=\frac{\lambda_x J_y}{\lambda_y J_x}, \tag{1}$$

where f represents the spectral exciting power,[2] i.e. $f_{yx}d\lambda_y$ is the emission of fluorescent light per unit volume of wave-length between λ_y and $\lambda_y+d\lambda_y$ when the fluorescing substance is illuminated with a density unity of exciting radiation of wave-length λ_x, f_{xy} is the same thing with the wave-lengths interchanged, and J_x, J_y are the densities of black-body radiation at these two wave-lengths. This equation is remarkable

[1] E. H. Kennard, Phys. Rev. **28**, 672 (1926).

[2] *Note.* The term "exciting power" is applied by Nichols and Merritt (Phys. Rev. **31**, 381 (1910)) to the quantity f/a where a is the absorption. The usage adopted here seems to be a little more in harmony with the common use of the term "power", which usually refers to a determining factor that is directly and readily controlled and measured, such as the exciting intensity in the present case. Perhaps the ratio f/a might be called the "spectral efficiency" of excitation.

in that it contains no unknown constants whatever. If such an equation could be shown to hold for the fluorescence of liquid and solid substances, it should constitute a distinct step forward toward a theoretical understanding of these phenomena; in particular, it would give quantitative support to the familiar suggestion that the great breadth of the bands is due in some way to the energy of thermal agitation. The equation, in an older but substantially identical form, was found to agree with existing data on eosin and resorufin.[3] The purpose of the present investigation was to test its validity on fluorescein, in which the shape of the fluorescence curve could not be assumed to be independent of the exciting wave-length.

The conclusion reached is that Eq. (1) is correct within the experimental errors as regards the implied variation of the anti-Stokes light with temperature, that it holds numerically wherever the anti-Stokes light is relatively bright, and at least approximates to the truth in all other cases tried.

I. Apparatus

In order to measure the spectral exciting power for wave-lengths close together it is necessary to adopt the relatively unusual procedure of resolving both the exciting light and the fluorescence. This necessitates the measurement of very weak light. A visual spectrophotometer was first tried but was found inadequate, the light being about ten times too faint even when the slits were made regrettably wide. The next simplest method appeared to be photography; so a "spectrograph" was improvised on an old mirror-spectrometer base, with a large flint prism, and with good projection lenses mounted, along with the slits, in wooden boxes fastened tightly to the spectrometer arms. It was found, however, that sufficient blackening could be obtained only by many hours of exposure; so with reluctance the troublesome method of photo-electric photometry was substituted.

For this purpose an old Dolezalek electrometer was converted into a "Compton," the original description[4] being followed except that the quadrants were made deeper. The instrument never worked really well; the worst of its irregularities finally ceased only when it was surrounded with a thick layer of cotton batting. The sensitivity was usually 10–15000 mm per volt at 250 cm. The photo-electric cell was one of the simplified Kunz type supplied by the Central Scientific Company; a special cell obtained from Professor Kunz himself was also tried but was not found much superior under the conditions of the experiment and was not used after being damaged by blue-glow discharges. Much time was lost in trying to compensate for a persistent

[3] E. H. Kennard, Phys. Rev. **11**, p. 37 (1918).

[4] A. H. and K. T. Compton, Phys. Rev. **14**, 85 (1919).

positive leak; for a high resistance, ionized air, alcohol, and India-ink lines on paper (K. T. Compton) were all tried but steadiness could not be obtained. Finally this drift was simply endured and in case of need partially compensated by allowing a little light to leak onto the cell from a lamp fed by a storage battery. The cell was mounted in an air-tight chamber, dried with P_2O_5, immediately under the electrometer; the spectrograph slit was placed about 20 cm from it, to allow a little freedom for manipulation, but the light path was carefully screened. By means of B-batteries and dry cells a voltage varying from 225 to 229.5 volts was applied to the cell. As the voltage rose above 226.5 volts the sensitivity rapidly increased but large irregularities began to appear in the response to light, hence the higher voltages were avoided as much as possible. The rate-of-drift method was employed, but proportionality of deflection rate, corrected for dark drift, was relied upon only in subsidiary observations.

The exciting light was furnished by a new Hilger constant-deviation spectrometer illuminated by a 400-watt tungsten lamp, whose plane-spiral filament was turned almost edge-on and then focussed on the slit through large lenses. The current through the lamp was carefully held constant, and the combined system was calibrated as to transmitted energy with a Coblentz thermopile and galvanometer. Tests made later showed no detectable change in spectral distribution over the range here used even when the blackening was carried to the point where the lamp usually failed.

Spectral calibration of both instruments was made with lines from a hydrogen-helium tube and from mercury and iron arcs, a reference point being inserted in the exit slits. The slits were then adjusted to the desired width (from 40 to 78A), entrance and exit slits of each instrument being set about equally wide in terms of transmitted wave-length, and readings were taken of the first appearance and of the final disappearance of the green mercury line as the setting was altered; the mean of these two readings was taken as the setting at which this line was transmitted centrally through the slits, and from it a correction to the calibration curve was computed for use in making settings upon other wave-lengths. Half of the difference of the two readings was taken as the slit width.

Since the sensitiveness of the electrometer could not be depended upon to remain constant, all principal measurements were made by a substitution method. The light from a tungsten lamp behind a ground-glass screen was reflected by a right-angle prism upon a magnesium-oxide block which could be slipped at will in front of the spectrograph slit. The lamp ran on a track whose "zero" was found by measurement, the distance through the prism being divided by the refractive index. The lamp with its ground-glass was calibrated with a Lummer-Brodhun

contrast spectrophotometer against a tungsten lamp whose color temperature at 97.3 volts had been determined at the Bureau of Standards. The magnesium block was also verified to be non-selective over the same range of wave-lengths. The extreme range of intensities covered in the observations was 200 : 1. To reduce the brighter intensities a filter was interposed in the exciting beam; the filters used consisted of photographic films between glass plates, in ratio steps of 2. Three of the most used transmissions were determined directly with the spectrophotometer in comparison with carefully measured sector discs run at 40 R.P.S.; the transmission of the other filters at the same wave-lengths was then compared with these by an obvious substitution method, and relative transmissions of all filters at other wave-lengths were observed in reliance upon proportionality of intensity and slit width (carefully corrected for zero error). The filters were found to be uniform over their surfaces within the accuracy of observation but they varied somewhat with wave-length.

The entire optical system was amply screened against stray light, both outside and by means of diaphragms inside the instruments.

The material employed was a sample of fluorescein kindly furnished by Professor E. Merritt; it had been specially purified in the Cornell laboratory of chemistry and was said to test 100% pure by analysis. A concentrated mother solution in absolute alcohol was prepared and from this working solutions were made by heavy dilution with the same solvent, the concentration being adjusted so that brilliant fluorescence was obtained without excessive absorption in the spectral region under observation.

II. "Anti-Stokes" Observations

Method of observation. For the principal observations designed to test Eq. (1), the intensity of the fluorescent light was increased by reflecting the exciting beam from a right-angle prism into the specimen and then taking the fluorescent light out backward, close to the prism, at an angle of 20–25° with the exciting beam. The paths of the two beams through the solution were thus made equal and the direct effect of absorption upon the result was eliminated; but absorption still had the disadvantageous effect of causing a much more rapid variation of intensity with wave-length than would occur with the beams at right angles. The specimen was contained in a glass tube about 18 mm in diameter and this was two-thirds enclosed on the sides by the upper end of a much thicker copper rod wound below with a heating coil, the exciting beam passing out through a slit in the copper in order to minimize scattered light, and a cylindrical lens of 7 mm focal length was inserted with the spectrograph slit and the useful part of the solution at conjugate foci. For the readings at room temperature a

thermometer was lashed to the rod near the tube (or at first merely placed over it on the tin screening). When the temperature was raised by means of the heating coil, a slender thermometer was passed down through a rubber cork into the top layer of the solution and a thick layer of wool was laid around the tube to check convection currents. In a subsequent test this thermometer was pushed down into the middle of the solution and then read 0.8° higher, so a correction of this amount was added to all "hot" readings. The temperature was easily held constant within half a degree.

To compare the reciprocal exciting powers for a chosen pair of wave-lengths, say λ_1 and $\lambda_2 > \lambda_1$, two similar half-sets of observations were taken, excitation being made at λ_2 in the first half-set and fluorescence observed at λ_1 these wave-lengths being then interchanged for the second half-set. The usual observational formula was *F D F F D C C D C C D C C D F F D F*, *F* denoting a drift due to fluorescence, *D* a dark drift, and *C* a drift due to the comparison lamp, which was set to give about the same effect as the fluorescence. From each complete set of observations the observed ratio of the exciting powers, $R = f_{21}/f_{12}$, was calculated. Let F_1, F_2 denote respectively the mean net rates of drift due to fluorescence in the two half-sets, L_1, L_2 the means of the net drifts due to the comparison lamp each multiplied by the square of the distance from the magnesium block, B_1, B_2 the relative spectral intensities of the comparison lamp at λ_1 and λ_2, S_1, and S_2 the relative intensities of the exciting beam at λ_1 and λ_2, and t_1, t_2 the transmissions of the filters used (usually none in the first half-set). Then

$$R \equiv \frac{f_{21}}{f_{12}} = \frac{F_2 L_1 B_2 S_2 t_1}{F_1 L_2 B_1 S_1 t_2} \tag{2}$$

Theoretical values of R were then calculated from (1) with the assumption of Wien's law for J, so that

$$\frac{1}{R} = \frac{f_{12}}{f_{21}} = \frac{\lambda^6_2}{\lambda^6_1} e^{-\alpha(\lambda_2 - \lambda_1)} \tag{3}$$

where $\alpha = 1.435/T\lambda_1\lambda_2$, T being the temperature of the fluorescing substance. A large correction for slit-width is, however, necessitated by the rapid diminution of the anti-Stokes light with decreasing wave-length. Entrance and entrance slits being equal, the spectral transmission of either instrument is represented as a function of wave-length by an isosceles triangle whose base is twice the spectral slit-width, w, and can be written $k(1 - |\lambda - \lambda_0|/w)$, where λ_0 is the central wave-length and k is a constant. The amount of light issuing from the spectrograph when the central wave-length of excitation is λ_2 and the

spectrograph is set to transmit centrally a wave-length λ_1 will therefore be

$$F_{12}=k'\int_{\lambda_1-\epsilon}^{\lambda_1+\epsilon}\int_{\lambda_2-\eta}^{\lambda_2+\eta} f_{1'2'}S_2'\left(1-\frac{|\lambda_1'-\lambda_1|}{\epsilon}\right)\left(1-\frac{|\lambda_2'-\lambda_2|}{\eta}\right)d\lambda_2'd\lambda_1'$$

where $f_{1'2'}$, S_2' denote respectively the exciting power and the spectral intensity of the exciting beam for wave-lengths λ_1' and λ_2', and ϵ, η are the respective slit widths of the two instruments. Putting $f_{1'2'}=f_{2'1'}\exp[-\alpha(\lambda_2'-\lambda_1')]$, in accordance with (3) but omitting the λ factors as inconsequential in the present connection, and then expanding f and S, we have

$$F_{12}=k'\int_{\lambda_1-\epsilon}^{\lambda_1+\epsilon}\int_{\lambda_2-\eta}^{\lambda_2+\eta}\left[f_{21}+(\lambda_1'-\lambda_1)\frac{\partial f_{21}}{\partial\lambda_1}+(\lambda_2'-\lambda_2)\frac{\partial f_{21}}{\partial\lambda_2}\right]\cdot \tag{4}$$

$$\left[S_2+(\lambda_2'-\lambda_2)\frac{\partial S_2}{\partial\lambda_2}\right]e^{-\alpha(\lambda_2'-\lambda_1')}\left(1-\frac{|\lambda_1'-\lambda_1|}{\epsilon}\right)\left(1-\frac{|\lambda_2'-\lambda_2|}{\eta}\right)d\lambda_2'd\lambda_1'.$$

If the wave-lengths are now interchanged on the two instruments, the issuing light becomes, with sufficient approximation,

$$\begin{aligned}F_{21}&=k'\int_{\lambda_1-\epsilon}^{\lambda_1+\epsilon}\int_{\lambda_2-\eta}^{\lambda_2+\eta} f_{21}S_2\left(1-\frac{|\lambda_1'-\lambda_1|}{\epsilon}\right)\left(1-\frac{|\lambda_2'-\lambda_2|}{\eta}\right)d\lambda_2'd\lambda_1'\\&=k'\epsilon\eta f_{21}S_2.\end{aligned} \tag{5}$$

Carrying out the integration in (4) and then dividing (4) by (5), we find

$$\frac{F_{12}}{F_{21}}=\frac{1}{R}=e^{-\alpha(\lambda_2-\lambda_1)}\frac{4}{\alpha^4\epsilon^2\eta^2}(\cosh\alpha\epsilon-1)(\cosh\alpha\eta-1) \tag{6}$$

$$\left[1+\frac{1}{\alpha f_{21}}\frac{\partial f_{21}}{\partial\lambda_1}\left(\alpha\epsilon\coth\frac{\alpha\epsilon}{2}-2\right)-\left(\frac{1}{\alpha f_{21}}\frac{\partial f_{21}}{\partial\lambda_2}+\frac{1}{\alpha S_2}\frac{\partial S_2}{\partial\lambda_2}\right)\left(\alpha\eta\coth\frac{\alpha\eta}{2}-2\right)\right].$$

The reciprocal of the right-hand member of (6), with the exponential factor omitted, was applied as a correction factor to the theoretical values of R. Approximate values of the derivatives of f_{21} as modified by absorption, which is obviously what is required in the formula, were obtained from subsidiary observations in which λ_1 and λ_2 were varied; in most of these, no allowance was made for the (moderate) spectral variation of sensitiveness of the observing system. The bracket in (6) containing these derivatives usually differed from unity by $1-3\%$ (maximum, 10%) and the entire correction factor ranged from 0.86 to 0.95. Rough estimates indicated that the effect of higher derivatives of f was very small.

An attempt was made also to estimate another source of error, that due to light scattered inside the instruments. Such light will tend always to make the anti-Stokes light appear too strong and so to diminish the observed value of R, and it is particularly serious in these observations because of the relative faintness of the light under observation. Before taking any of the final data, the green light from a mercury lamp, isolated by absorbing glasses, was passed into the Hilger spectrometer and the amount of light issuing through the slit for various settings of the drum was determined photometrically in comparison with a direct beam from the lamp. Light from the spectrometer was then reflected into the spectrograph for a similar test upon that instrument, correction being now made for the scattering in the spectrometer. As an example, the light scattered through the slit when set 120A away from the entering wave-length came out about 0.00044 of the light transmitted without scattering, for both instruments; at 200A it was half as much. An approximate integration was then made, from the source calibration curve and from fluorescence and exciting power curves obtained in a separate rapid survey, to find the resulting error in R, this being done for only a few pairs of wave-lengths and interpolation being then employed for the others. The results ought to be correct at least within fifty percent.

A point clearly brought out by these calculations and not always properly appreciated is that the scattering in the observing instrument may for some settings be a more serious source of error than that in the exciting instrument because of the large amount of fluorescent light which is passing through and which is much stronger than the wave-length actually being observed.

The final results are given in Table I. λ_1 and λ_2 are the two wave-lengths for each set, I is a rough estimate of the intensity of the "anti-Stokes" light, R is the observed value of that quantity (anti-Stokes exciting power divided into the inverse power), ρ is the ratio of the theoretical value of R, corrected for slit width but not for scattering, to the observed value, and Sc is the estimated percent increase in ρ caused by scattered light. The same specimen was used throughout the first long series of observations at room temperature; for the series at a higher temperature, which followed, a fresh dilution was made from the mother solution with one drop of NaOH added, and fresh portions of this were taken at intervals; and the latter material was also used for the final five sets except that for the very last set six drops of NaOH were added to the specimen under observation. Other sets in considerable number were rejected because of some known or suspected error in the adjustments, but consistency in the policy as to rejections, independently of whether the theoretical equation was confirmed or not, has been preserved.

TABLE I

Results on the violation of Stokes' law

λ_1	λ_2	I	R	ρ	Sc	λ_1	λ_2	I	R	ρ	Sc
(Temperature, 20.0–24.4°)						(Temperature, 60.2–64.4°)					
5320–5469		8	8.23	1.02	12	5316–5469		11	4.67	1.53	9
5265–5469		8	24.3	.89	13	5268–	"	9	11.6	1.20	9
5219–5469		9	38.9	1.19	12	5176–5365		24	12.2	1.05	3
5180–5469		6	83.6	1.12	13	5132–5316		37	11.0	1.11	2
5176–5469		6	68.3	1.38	12	5132–5268		83	6.66	1.00	2
5114–5469		3	290.	.90	14	5089–	"	51	13.3	.96	2
5134–5269		54	7.37	1.08	2	5048–	"	25	23.7	1.02	3
5091–5269		34	16.4	1.01	3	5009–	"	20	43.3	.96	4
"	"	33	16.2	1.08	3	4951–	"	7	92.	1.17	11
5050–5269		17	29.3	1.13	4	4916–	"	4	115.	1.65	15
"	"	14	31.5	1.06	4	5048–5178		89	6.68	1.02	2
5010–5269		9	57.0	1.16	6	5009–	"	47	10.8	1.13	3
"	"	8	55.8	1.25	6	4971–	"	24	19.8	1.15	5
4976–5269		6	77.3	1.61	9	4936–	"	16	31.2	1.26	8
5090–5200		60	6.45	.95	2	4898–	"	7	55.	1.33	10
5050–5200		22	16.4	.77	4						
5011–5200		24	14.8	1.67	13	(Temperature, 24–25°)					
4976–5200		10	32.3	1.42	8	5089–5268		19	15.5	1.14	3
4938–5200		4	113.	.82	12	5048–5200		27	11.6	1.07	3
5011–5133		43	7.47	1.09	3	5176–5364		11	17.8	1.03	3
4976–	"	26	13.2	1.18	5	5177–5330		14	9.58	1.12	2
4940–	"	11	25.7	1.14	7	"	"	54	9.97	1.08	2

A glance at the results shows at once that the theoretical law expressed by Eq. (1) must at least come near to the truth. The discrepancies seem to be correlated chiefly with the intensity of the anti-Stokes light and not with either spectral position or temperature; a few of the largest were no doubt due to an undetected blunder in adjustment. In Table II the results are divided into three groups according to the intensity of the anti-Stokes fluorescence and mean values of ρ and of Sc are given for each group; the number of sets in the group is given in parentheses.

TABLE II

The data of Table I averaged by groups.

I	Cold			Hot		
		ρ	Sc		ρ	Sc
25–60	(8)	1.067	2.6%	(6)	1.039	2.5%
12–24	(6)	1.15	3.3	(4)	1.104	5.0
3–11	(13)	1.15	10.	(5)	1.38	11.

Sources of error. The most serious source of error next to scattering undoubtedly lies in the spectral settings. An error of only one angstrom in the assumed difference in wave-length between the slits of the two instruments makes a difference of about 1.7% in the value of ρ. An accuracy of this order was striven for with more or less success in the calibrations, but it is doubtful whether subsequent settings are reliable

to this extent. The average deviation from their mean of the six electrometer readings ranged in different sets from 2 to 8%, so that the Accidental error in ρ would be at least several percent.

No correction is required for absorption, since the paths of exciting and of fluorescent light through the solution were equal and the total effect of absorption would therefore remain the same when the wave-lengths were interchanged. As a check, a very concentrated solution gave $R=13.81$ for the 5268–5089 ratio, whereas the same solution diluted to half and then to quarter strength gave $R=15.28$, 15.20. The strength usually employed lay between the last two. On the other hand, there does exist the possibility of a systematic error arising from the fact that the different wave-lengths coming from the source were not distributed spatially in quite the same manner in the solution; and an analogous inequality existed in regard to the fluorescent light. The resulting error is hard to estimate. In any case, it can hardly explain the systematic trend of the observed discrepancies, for it should be equivalent to a fixed shift in wave-length and so should produce the same percent of error in all ratios. Furthermore, a single set of readings taken later on the 5245–5090 ratio, under unfavorable conditions, with the exciting light taken out from a square cell at right angles to the exciting beam, gave $\rho=1.06$, in good agreement with the previous results.

Conclusion. In view of all these sources of error the conclusion seems justified that the first group of observations in Table II definitely support the theoretical equation given in (1) and the second group, $I=12$ to 24, are not inconsistent with it. A doubling of the allowance for scattered light would on the average pretty well cover all of the discrepancies; and it is a fact that a few imperfect tests with absorbing screens suggested considerably larger effects due to this cause. The third group of results are therefore not decisively inconsistent with (1) and show that this equation at least comes pretty near to the truth even when the anti-Stokes light is very weak.

The factor λ_z/λ_y in (1) is a characteristic contribution from quantum theory and its experimental verification would therefore be of particular interest. Here we can only say that the omission of this factor would make the observed agreement *worse* by 2–4%.

III. Fluorescence, Excitation and Absorption Curves

In August, with the photo-electric system working poorly, a rapid survey was made of the relative exciting powers for the solution of fluorescein that had been used in the "hot" observations. The material was put in a square cell and viewed near one corner at right angles to the exciting beam, a correction (0–20%) being made for absorption. The coefficient of absorption was determined with the spectropho-

tometer by the usual method of observing slit-widths first with the solution and then with pure alcohol in the cell and taking the logarithm of the ratio of these readings; the slit zero was found by measuring the known transmission of the 0.5 filter with extremely narrow slits. The smallest transmission through 2 cm of the solution came out about 10%. The spectrometer slit was not over 100A wide.

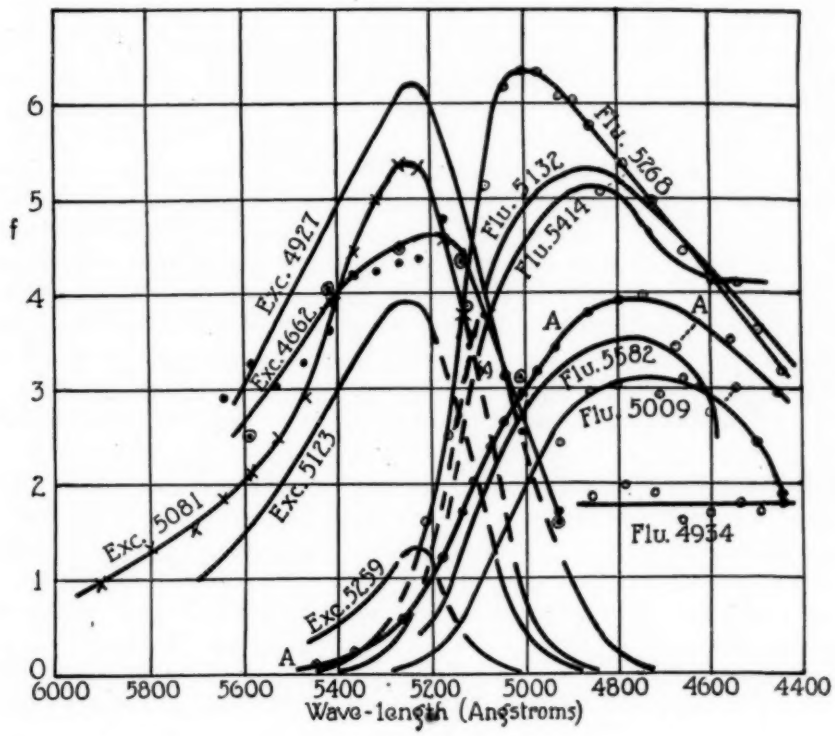

FIG. 1.

The results are shown in Fig. 1, curve *AA* giving the absorption on an arbitrary scale. The fluorescence curve was determined, using the comparison lamp, for excitation at 5081A (× in the figure representing in part the means of several repetitions), and at 4662 (dots in the figure, the dots in circles denote values obtained from the excitation curves), also a few points at 4787. Excitation curves were then found, by simply varying the exciting wave-length and assuming proportionality of deflection rate and fluorescent energy, for fluorescence at 4934, 5009, 5132 (points not shown in figure), 5268 (more or less repeated), and 5132 and 5414 (points not shown). The scale factors of the various curves were assumed to be unknown and were adjusted so as to secure

the best harmony between all of the results. In this way there was obtained a set of numbers, some in duplicate, proportional to the true exciting power, f, for various pairs of wave-lengths; these are plotted twice over in the figure, first, as fluorescence curves (left) each giving the spectral intensity of fluorescence of various wave-lengths excited in unit volume by unit density of energy of a given wave-length, and, second, as excitation curves (right) each giving the spectral intensity of fluorescent emission from unit volume of a certain wave-length excited by unit energy density of various wave-lengths, all on the same arbitrary scale. Additional values calculated from Eq. (1) were used to extend each set of curves on one side beyond the region of direct observation.

Circumstances made it impossible to secure more than two electrometer readings on each point, with some checking back to guard against systematic change of conditions, consequently the observed parts of the curves may be in error by as much as 6% of the largest value of f shown (the upper parts of the curves marked "Exc. 5081" and "Fluo. 5268" being perhaps twice as accurate). Nevertheless the data seemed to possess at least temporary interest because they suffice to establish the following conclusions:

(1) The fluorescence curve is not constant in shape. Not only does it draw in its toes toward the violet as the exciting wave-length encroaches upon it, thus preserving the validity of Eq. (1), but the center also rises, until the exciting wave-length reaches 5000A, after which the whole curve drops rapidly. This result is not necessarily in conflict with earlier data of Nichols and Merritt,[5] who found no change of shape for a solution in *water*; their material was also doubtless less pure. Those authors found,[6] however, for an alcoholic solution two maxima at 5340 and 5500, resp., with shoulders at 5240 and 5680, whereas here there is a single maximum at 5240 ± 30A. This difference may be due either to greater purity of the material used in the present investigation or to the fact that those authors appear to have excited with much shorter wave-lengths.

(2) The wave-length of maximum excitation shifts from 4730 ± 80A for fluorescence at 5000 or at 5600 to 5000 ± 40A for fluorescence at 5268.

(3) For a particular wave-length of fluorescence, excitation and absorption are obviously not (always) proportional. A rough integration yields the further result that the total fluorescence increases in relative strength, by a total amount of 28%, as the exciting wave-length rises from 4800 to 5100, after which it drops sharply; but too great reliance cannot be placed upon this result because the long-wave

[5] Nichols and Merritt, Phys. Rev. **18**, 403 (1904).
[6] Nichols and Merritt, Phys. Rev. **32**, 38 (1911).

part of the fluorescent spectrum is incompletely represented. Vavilov found[7] total fluorescence and absorption to be proportional for an aqueous solution of fluorescein; but results similar to those described here were found by Valentiner and Rössiger.[8]

These results would all find qualitative explanation if there were in reality two fluorescence bands of invariable form with maxima close together, one being a broad band with a broad excitation curve having its maximum around 4730 and the other a narrower but stronger band with a narrow excitation curve at about 5000A.

A more thorough study of the exciting power in fluorescein would seem to be well worth while. Probably for this purpose the far greater rapidity of visual photometry as compared with the photo-electric method would amply compensate for the trouble of finding enough line sources or good screens so that spectral resolution of the source light could be avoided.

This investigation was made in the physical laboratory of Cornell University and was supported by a grant from the Heckscher Research Council. The assembling of apparatus and most of the observational work was done by Mr. L. S. Taylor, who acted as research assistant under the grant, and the author is deeply indebted to him for his skilful handling of the instruments and for his cheerful persistence in the face of difficulties. The author is also indebted to many of his colleagues in Cornell for innumerable courtesies during the progress of the work.

GÖTTINGEN,
November 15, 1926.

[7] S. I. Vavilov, Phil. Mag. **43**, 307 (1922).
[8] Valentiner and Rössiger, Zeits. f. Physik, **36**, 81 (1926).

A COMPOUND INTERFEROMETER FOR FINE STRUCTURE WORK

By William V. Houston*

Abstract

The overlapping of orders in a Fabry-Perot interferometer can be avoided by using two interferometers in series. The fundamental equation shows that the dispersion is independent of the plate separation, while the distance between orders is inversely proportional to it. Thus an instrument with a small separation may be used as a preliminary filter to eliminate some of the orders in one of larger separation. This will not affect the fine structure pattern, and the resolution will be even greater than that due to the larger separation. Such an instrument has been built and satisfies the predictions of the theory. A plate, taken with the green line of mercury, is shown to illustrate the effect of the preliminary interferometer.

As an instrument for studying spectral fine structure the Fabry-Perot interferometer has several advantages over other high resolution instruments. It has a uniform intensity distribution over the whole image;[1] it is free, if properly adjusted,[2] from the errors due to the overlapping of two members of a close doublet; and it can be used to measure absolute wave-lengths. Furthermore, the distance between orders, measured in frequency units, is independent of the wave-length, so that it is useful in the identification of spectral series. The outstanding difficulty, however, is that when the plates are separated far enough to give high resolution, the successive orders are so close together that the patterns overlap. It is to overcome this difficulty, without sacrificing the advantages, that this combination of two interferometers has been devised.

Light is transmitted through a Fabry-Perot interferometer with maximum intensity if it is incident at an angle θ such that $2d \cos\theta = n\lambda$, where d is the distance between the plates, λ is the wave-length, and n is an integer. Thus the distance between orders is given by

$$d(\cos\theta)/dn = \lambda/2d \qquad (1)$$

and the dispersion by

$$d(\cos\theta)/d\lambda = n/2d = \cos\theta/\lambda \qquad (2)$$

which is independent of d. The resolving power is proportional to the order of interference n, and hence to the separation d. Thus, to get a high resolving power it is necessary to use a large d. This brings the

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[1] This is particularly true as contrasted with the echelon.

[2] W. V. Houston, Astrophys. J., **64**, 81 (1926).

successive orders close together, and sometimes causes overlapping. But, if light is incident on the interferometer at an angle θ_0 corresponding to $n=n_0$, and no light is incident at the angle θ_1 corresponding to $n=n_0+1$, it is evident that no light can be transmitted at this angle. Thus this order will be missing from the transmitted pattern.

If an interferometer of small separation is used as a preliminary filter, it will transmit light to the second in certain directions only; but since the dispersion is independent of the separation, the fine structure pattern will be transmitted or destroyed as a whole. Thus if the separation of the second is twice that of the first, every other order will be transmitted, and the fine structure pattern will not be disturbed. Furthermore, the resolution will be even greater than with the second interferometer alone.

The Complete Theory

Consider the four lightly silvered surfaces 1, 2, 3, and 4 in Fig. 1. Surfaces 1 and 2, and 3 and 4 are accurately parallel to each other,

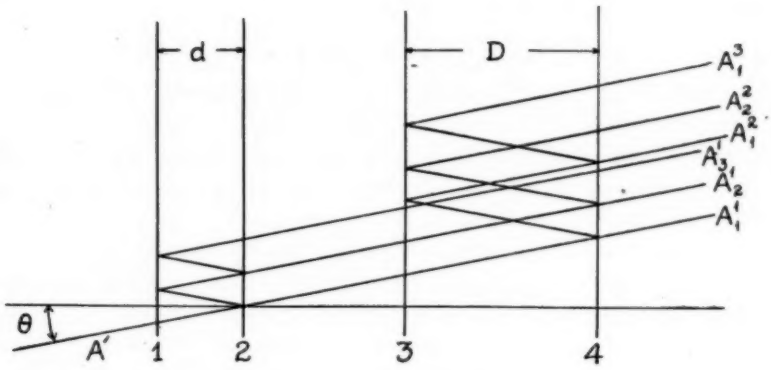

Fig. 1.

while 2 and 3 are inclined at just enough of an angle to prevent interference between them. This angle must be so small that the axes of the two instruments are practically together. Let A' be the incident amplitude, and A the resultant emerging amplitude. Let the amplitudes due to successive reflections be indicated by A_m^n where the subscript indicates reflections between the first surfaces, and the superscript indicates reflections between the second pair. Let R be the intensity coefficient of reflection and let $R=\rho^2$. We may neglect the absorption since it can be applied as a constant factor to the resultant intensity. From Fig. 1 it is evident that we have

$$A_1^1=A'(1-\rho^2)^2 \qquad A_2^1=A_1^1\rho^2 \qquad A_3^1=A_1^1\rho^4$$
$$A_1^2=A_1^1\rho^2 \qquad A_2^2=A_1^1\rho^4 \qquad A_{m+1}^{n+1}=A_1^1\rho^{2\,(m+n)}$$

Then the resultant amplitude is given by

$$A = A_1^1 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \rho^{2(m+n)} \cos(wt - mb - nB) \tag{3}$$

where $B = 4\pi D \cos\theta/\lambda$ and $b = 4\pi d \cos\theta/\lambda$. Let $wt - mb = M$ and the summation becomes

$$\begin{aligned} A &= A_1^1 \sum_{m=0}^{\infty} R^m \sum_{n=0}^{\infty} R^n \cos(M - nB) \\ &= A_1^1 (1 - 2R\cos B + R^2)^{-1} \sum_{m=0}^{\infty} R^m [\cos(wt - mb) \\ &\quad - R\cos(wt - B - mb)] \end{aligned} \tag{4}$$

Carrying out the second summation and introducing a phase constant we have

$$A = A_1^1 (1 - 2R\cos B + R^2)^{-1/2} (1 - 2R\cos b + R^2)^{-1/2} \cos(wt + \psi). \tag{5}$$

Squaring this, the intensity is given by

$$I = (A_1^1)^2 / (1 - 2R\cos B + R^2)(1 - 2R\cos b + R^2) \tag{6}$$

Equation (6) is just the product of the corresponding equations for the two separate interferometers. This justifies the process, used in the qualitative theory, of considering the action of the second instrument on the light transmitted by the first, without reference to the interference processes in the first.

If the values of d and D are such that $2d\cos\theta = n\lambda$, and $2D\cos\theta = m\lambda$, both instruments will transmit a maximum at the angle θ. However, the next maxima of the two instruments will not coincide, in general, and so both will be greatly decreased in intensity. The next maxima that do coincide will be determined by the ratio of D to d. For example, if $d = D$ the pattern transmitted by the two will be the same as for one interferometer, but, as will be shown later, the maxima will be sharper. If $D = 2d$, the separation of orders is that due to the separation d, while the resolving power is that due to the separation D, i.e., only every other order of the second instrument is transmitted. If $D = 3d$, only every third order is transmitted. In all these cases the dispersion is the same so that computations of absolute wave-length and frequency difference can be carried out as with the simple instrument. This constitutes the principal advantage of the air interferometer over instruments in which the path difference is wholly or partly in glass.

To determine the resolving power we may assume that two fringes can be recognized as distinct if their maxima are separated by a distance equal to the width of one image where its intensity has dropped to one half its maximum value. The computations, of course, assume

two purely monochromatic lines of equal intensity. We then wish to find the value of B for which the intensity drops to 1/2. In the case of a single interferometer we have

$$1-2R\cos B+R^2=2(1-R)^2 \tag{7}$$

and hence

$$B=\cos^{-1}\{1-(1-R)^2/2R\} \tag{8}$$

The spectral range, or the difference in wave-length corresponding to the distance between orders, is given by the fundamental equation to be $\lambda^2/2D$. Hence

$$\lambda/\Delta\lambda=2\pi D/\lambda\cos^{-1}\{1-(1-R)^2/2R\} \tag{9}$$

$2D/\lambda$ is the order of interference n so we have

$$\lambda/\Delta\lambda=\pi n/\cos^{-1}\{1-(1-R)^2/2R\} \tag{10}$$

For $R=0.75$ this gives the resolving power as about $11n$.

For the two interferometers we have

$$(1-2R\cos B+R^2)(1-2R\cos b+R^2)=2(1-R)^4$$

or,

$$\cos B+\cos b-2R(1-\cos B)(1-\cos b)/(1-R)^2=[4R-(1-R)^2]/2R \tag{11}$$

B and b will both be small enough so that the cosines may be represented by the first two terms of their series so that we have

$$(1+r^2)b^2+Rr^2b^4/(1-R)^2=(1-R)^2/R \tag{12}$$

where $r=D/d=B/b$. Here again we may neglect the fourth power of b, unless R is very large, so that

$$b=(1-R)/(1+r^2)^{1/2}R^{1/2} \tag{13}$$

Then we have

$$\Delta\lambda=\lambda^2(1-R)/2\pi d(1+r^2)^{1/2}R^{1/2}$$

or

$$\lambda/\Delta\lambda=n\pi R^{1/2}(1+r^2)^{1/2}/(1-R) \tag{14}$$

Thus the resolving power of the combination is equal to that of the smaller interferometer multiplied by $(1+r^2)^{1/2}$. When $R=0.75$ and $r=1$ the resolving power is about $15n$.

Fig. 2 shows the shape and the separation of successive maxima when $D=3d$ and $R=0.75$. The two small maxima represent the remnants of the maxima cut out by the smaller instrument. These will be smaller as R increases, and also as they are farther from the principal maxima. This puts a limit to the value of r that can be used, since when r is large these spurious maxima will be closer to the principal ones and hence they will be stronger. When dealing with a fine structure in which the satellites are faint compared with the principal line, care must be taken not to mistake these maxima for satellites. If plates are taken with two different values of r, the true satellites can be

distinguished easily by the fact that their positions will be the same on both plates.

Description of the Instrument

An instrument of this kind has been built in the machine shop of this laboratory under the direction of Mr. Julius Pearson. An attachment was made for the interferometer previously built, so that the preliminary interferometer can be clamped to the frame of the other.

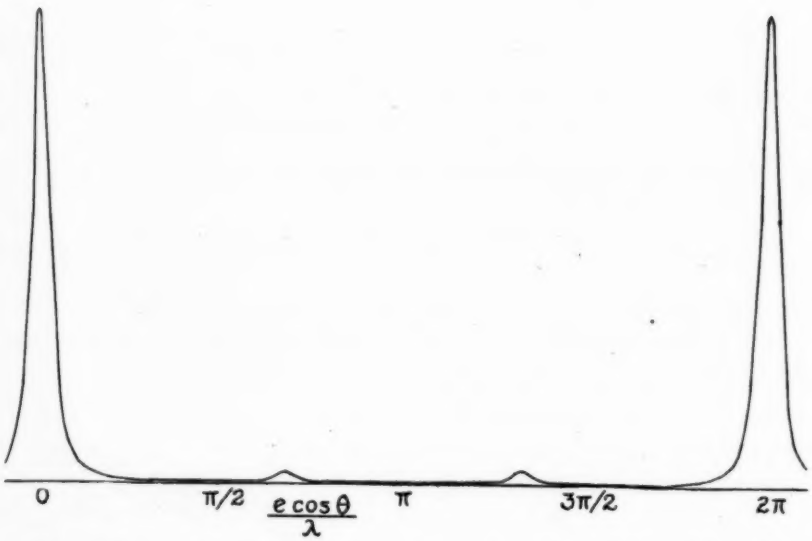

Fig. 2. Shape and separation of successive maxima when $D=3d$ and $R=0.75$.

This clamp carries a steel plate which can be rotated about two axes to set the optical axes of the two instruments together. This plate then carries one mirror which slides back and forth and can be fastened by set screws, and another which can be made parallel to the first. All the adjustments are made by screws working at the ends of levers which are held tightly against the screws by springs.

It has been found possible to make the necessary adjustments as follows. With the preliminary interferometer removed and the other set at about the separation to be used, the latter is adjusted until the plates are parallel. The other interferometer is then attached and its fringes are viewed from the side by means of a totally reflecting prism. In this way its plates can be made parallel. When the prism is removed the transmitted light shows the ring system of each interferometer as well as regions of brightness where the two systems coincide. If the axis of the preliminary interferometer is then adjusted until these regions of brightness are circles concentric with the other ring systems,

the instrument is in adjustment. To make one separation an integral multiple of the other the movable interferometer is opened or closed to make the circles of bright rings move toward the center. As the desired separation as approached these regions become wider until they cover the whole field. A white light source is then put in and the adjustment continued until the colored fringes appear. When the white central fringe appears the desired point has been reached. This phenomenon of white light fringes was first used by Perot and Fabry[3] in the measurement of length.

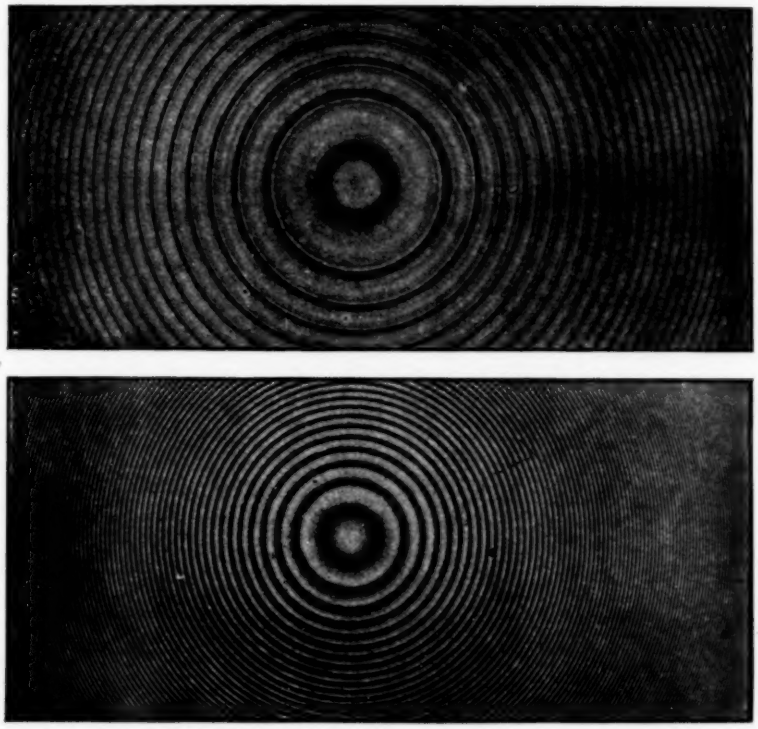

Fig. 3. Fringe system of the mercury line: above, through double interferometer; below, through the single interferometer.

A preliminary trial with rather inferior plane surfaces has given the plates reproduced in Fig. 3. The upper photograph shows the fringe system given by the green mercury line when one separation was about 3 mm and the other was about 9 mm. The lower photograph shows the same line through the 9 mm interferometer only. The overlapping of the fine structure patterns in this case causes the main line to appear fuzzy at the edges.

[3] Perot and Fabry, Ann. chim. et phys. **7**, 16 (1899).

Preparations are under way to apply this instrument to the study of the hydrogen doublets and to other fine structure problems. It should be valuable in the study of hyper-fine structure, such as that of mercury. The principal disadvantage is that a good deal of light is absorbed in passing through the four silver films, but this is characteristic of all high resolution instruments. On the other hand, this arrangement offers all the advantages of a fine grating in the direct measurement of fine structure, and is superior to the grating in resolving power and in the determination of absolute wave-lengths.

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November 15, 1926.

AN ABSOLUTE METHOD FOR MEASURING THE VELOCITY OF FLUIDS

By H. E. Hartig and H. B. Wilcox

Abstract

Trains of sound waves of a definite frequency, emitted by sound sources which are separated by a known distance, are sent up and down a pipe in which flows a stream of fluid whose velocity is required. Anti-nodes formed in the region between the sound sources undergo a shift the magnitude of which depends upon the velocity of the fluid. By using interrupted wave trains the effects of reflections at the ends of the pipe are eliminated. The meaning of the velocity measured by this method is considered when the flow of the fluid is turbulent. Experiments on air flow show that the anti-nodes are sharply defined, stationary with time, and occur on planes normal to the axis of the pipe. It is concluded that the average velocity as calculated from the sound shift method differs by a negligibly small amount from the average velocity obtained by dividing the total flow per second past a section, by the area of the section. A smoke cloud introduced into the air stream and timed over a known distance yields results which are compared with those obtained from the sound shift method.

HUGUENARD[1] has described an absolute method for measuring the flow of air through pipes. The method consists essentially in photographing a sound wave produced by one spark in moving air by the light of a second spark which follows at a known interval of time.

The method described in this article is based on the nodal shift occurring when a medium in which standing sound waves exist is set in motion.

I. Description and Theory of Method

Consider a plane sound wave of frequency f, whose amplitude varies harmonically with time, originating at A and traveling in the positive x direction in a stationary medium; and a second plane wave of the same frequency and maximum amplitude originating at B and traveling in the negative x direction. Then stationary planes of zero pressure variation, or anti-nodes, are created. These anti-nodal planes are perpendicular to the x axis and are equally spaced one-half wave-length apart.

If now the medium moves in the positive x direction with velocity v the anti-nodes will shift in the direction of motion of the medium. The magnitude of the shift depends upon the distance between the sources at A and B, the velocity of propagation of sound in the stationary medium, and upon the velocity of the medium. In order to calculate the velocity of the medium it is sufficient to know the magnitude of the

[1] Huguenard, Comptes rendues **117**: pp. 744–746 (Oct. 22, 1923).

shift, the distance between the sound sources, the velocity of propagation of sound in the stationary medium, and the form of the function which connects these quantities. This relation may be established as follows.

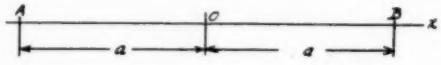

Fig. 1.

Let the origin be taken midway between the sources A and B which are separated by a distance $2a$ (Fig. 1). Then if p_1 be the increase in pressure at any point x at time t due to the wave originating at A, we have

$$p_1 = p_0 \sin 2\pi f(x+a)/[(V+v)-t]$$

where p_0 is the maximum pressure variation and V is the velocity of propagation of sound in the stationary medium. The pressure variation p_2 due to the wave which originates at B is given by a similar expression with appropriate changes in sign.

The total pressure variation at all points between $-a$ and a is

$$p_1+p_2 = 2p_0 \sin \pi f\left(\frac{x+a}{V+v}+\frac{x-a}{V-v}\right)\cos \pi f\left(\frac{x+a}{V+v}-\frac{x-a}{V-v}-2t\right).$$

The right hand member of this equation will be zero for all values of t provided that x lies between $-a$ and a, and satisfies the equation

$$\sin \pi f\left(\frac{x+a}{V+v}+\frac{x-a}{V-v}\right)=0.$$

From this equation

$$x=\frac{n(V^2-v^2)}{2fV}+\frac{av}{V}, \quad \pm n=0,1,2\cdots.$$

When v is zero the anti-nodes are located at points given by $X = nV/2f$.

The shift s in the position of the anti-nodes is, therefore,

$$s = av/V - n\lambda v^2/2V^2,$$

where λ is the wave-length in the stationary medium. When n is zero, that is for the anti-node at the origin, the velocity is given without approximation by $v = Vs/a$. If, however, observations are taken at points at which n is not zero and provided that v/V is small this equation gives results which are only slightly in error. If, moreover, observations of shift are taken upon a series of anti-nodes for which the algebraic sum of the n's is zero, the number obtained by averaging these values will be equal to the shift corresponding to $n=0$.

To determine V, the velocity of sound, it is sufficient to measure the distance d between anti-nodes when the medium is at rest. Then $V = 2fd$, where the frequency f must be known.

Thus far it has been assumed that the fluid is flowing with constant velocity at every point in the pipe. In an actual case the flow is likely to be turbulent. It was shown by experiments on the flow of air in a pipe having an internal diameter of four inches that the anti-nodes were sharply defined on planes normal to the axis of the pipe and did not change position with time although the air flow was known to be turbulent. It is inferred from this result that the average axial component of the velocity at any instant is the same along any line of sufficient length and parallel to the axis, and that the average velocity at any instant along such a line does not change with time. The average velocity referred to is the velocity obtained by the sound shift method, and is defined by

$$v_1 = d \Big/ \int_0^d \frac{dx}{v_0 + \Delta v + V}$$

where V is the velocity of sound in the stationary medium and $v_0+\Delta v$ is the instantaneous axial component of the velocity of the medium at any point, the integration being carried along the axis over a length d.

The average velocity necessary in calculating the volume of fluid flowing past a section of the pipe per second, is defined by

$$v_2 = (1/At) \int_0^t \Big[\iint_A (v_0 + \Delta v) dA \Big] dt$$

where the double integral is extended over a normal section of the pipe.

When the velocity is a constant v_0 both of these definitions give v_0 as the average velocity. To compare v_1 and v_2 when $v_0+\Delta v$ is not constant

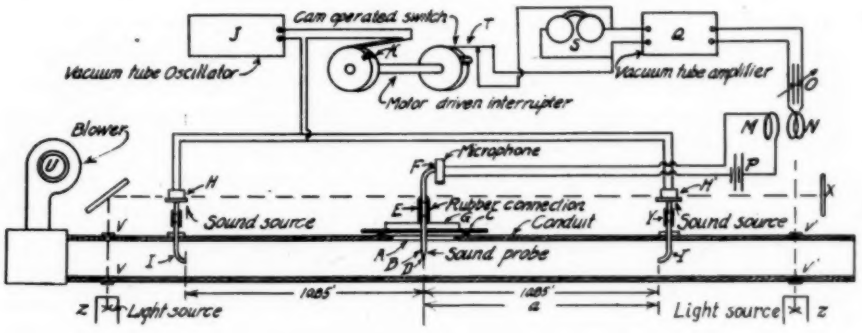

Fig. 2. Diagram of apparatus.

we shall make the following assumptions: (1) Along every line sufficiently long and parallel to the axis the instantaneous velocity of the medium is constant, $v_0+\Delta v$ for one-half the length of the line, and $v_0-\Delta v$ for the remaining half; (2) over every normal section of the pipe the velocity is constant, $v_0+\Delta v$ for a time $t/2$, and $v_0-\Delta v$ for an equal time.

Using the first assumption with the definition of v_1 we obtain $v_1 = v_0 - \Delta v^2/(v_0 + V)$. With the second assumption and the definition of v_2 we obtain $v_2 = v_0$.

With these rough approximations it appears that the two definitions give average values of velocity which differ by a small amount. In any event if Δv is small compared with v_0 the actual conditions approximate closely the ideal conditions for which the two definitions give identical results.

II. Description of Apparatus

The apparatus consists of a wrought iron pipe 4 inches in diameter and approximately 42 feet long, having a longitudinal slot A 18 inches long at the center. A sound probe B carried by a cover slide C projects through the slot to the center line of the pipe where it terminates in a narrow transverse slit D, the other end of the probe being connected by means of a short rubber tube E to the sound chamber of a microphone F. The slide C carries a pointer which allows its position to be read upon a fixed scale G graduated in hundredths of inches.

The sound sources are located at the quarter points of the pipe and consist of two telephone receivers H, H' which communicate by means of short rubber tubes with the bent tubes I. The sources are supplied with current by a Western Electric vacuum tube oscillator J. The current from the oscillator is established at regular intervals by an adjustable speed, motor-driven commutator K.

The battery P and the primary coil M which is inductively coupled with the coil N form a series circuit with the microphone F. The terminals of a tuned circuit consisting of the coil N and the variable condenser O, are connected to the input of an audio-frequency vacuum tube amplifier Q.

The listening receivers S are connected to the output of the amplifier. The receivers remain short circuited by the switch T except for a definite interval when the switch is opened by a cam on the shaft which drives the commutator K. The entire receiving apparatus was carefully shielded.

A current of air may be driven through the pipe by the motor-driven blower U.

The apparatus for the purpose of visually determining the fluid velocity consists of two light sources Z projecting beams of light through windows V, V' across the pipe, the light beams being directed by a mirror and lens system to an observing station X.

The operation of the apparatus is as follows: alternating current at a frequency of 2500 cycles per second operates sound sources H and H' at regular intervals of time which depend jointly upon the length of the contact segment of the commutator K and upon the adjustment

of its speed. In consequence of this current, the sound sources emit trains of waves of like frequency, which travel up and down the pipe. The amplitude of the two trains of waves is equalized by moving one or the other source in or out of the resonating connecting tubes Y, until the anti-nodes indicated at the receivers S are nearly perfect. A fine adjustment of amplitude is obtained by varying a resistance in circuit with one of the sources. The commutator K is used to avoid the superposition of waves set up by reflection at the ends of the pipe with the original waves, such combinations of original and reflected waves giving, as would be expected, anti-nodes of variable intensity and irregular spacing. Indeed, it was found that without commutation the anti-nodes shifted in an irregular manner when a current of air was passed through the pipe.

By changing the relative positions of the cam and short-circuiting switch it was observed that the time interval required for the disappearance of the musical character of a wave train corresponded to about one-half of a revolution of the cam shaft. The time allowed between listening to successive wave trains was approximately 0.4 sec.

On the same shaft with the commutator a cam operating a switch T renders the listening circuit inoperative except for the short time, about 0.02 sec. during which the undisturbed standing wave is being received by the probe B.

When a current of air is sent through the pipe the positions of the anti-nodes which were determined with the air at rest, are shifted in the direction of motion a distance s from which the average velocity of the air current is calculated as described.

III. Velocity by the Smoke Drift Method

The results obtained by the sound shift method were compared with independent determinations of the air velocity made by introducing a smoke puff into the air current and measuring the time required for the smoke cloud to drift with the current over a measured distance. A single observer with a stop-watch took all observations of the time during a run. This was effected by passing a beam of light through windows V in the pipe near its beginning and by means of a mirror and a lens system directing the beam to a screen located close to the observer stationed at a similarly illuminated opening V' at the other end of the pipe.

It was found that the smoke cloud elongated in passing through the pipe and a greater time was required for the cloud to pass the down-stream pair of windows than was required at the up-stream station.

The smoke drift method is similar to the color velocity method employed by Allen and Taylor[2] to determine the average velocity of

[2] Allen and Taylor, ASME Trans. **45**, 285 (1923).

water flowing in a pipe. Colored solution is introduced into the pipe and the passage of the solution between observing stations is recorded. The velocity obtained by timing the center of the colored mass between stations was found equal to that obtained by measuring the discharge. In view of the experience of Allen and Taylor it appears reasonable to assume that the time to be taken in the smoke drift method is that required for the center of the cloud to traverse the distance between the stations.

The constancy of the average air velocity was checked by a vane type anemometer. The anemometer readings during a run agreed to within one percent.

IV. Results

The results of two separate sets of determinations of the velocity of flow of air in a pipe are tabulated as follows:

	1st run	2nd run
Anti-node shift in cm (average of 5 readings)	$0.904 \pm .005$	$1.859 \pm .005$
Computed velocity in cm/sec	$94.2 \pm .6$	$193.5 \pm .6$
Velocity by smoke drift method (average of 18 readings)	95.4 ± 3.0	$195. \pm 4.5$

The velocity of sound in the pipe as determined from the average of five readings was 344.4 ± 0.6 meters per sec.

From their experience in conducting this investigation, the writers believe that the sound shift method will yield very accurate results in the measurement of the velocity of flow of gases in pipes, especially where a long straight column of the gas is available. Further work is being done in extending the sound shift method to the measurement of flow of water in pipes and open channels. Some preliminary work has been done to improve the accuracy of the smoke drift method by replacing the observer by an automatic recording device.

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Finally, we desire to express our appreciation to Dean Ora M. Leland of the College of Engineering for making funds available to procure needed equipment.

Engineering Laboratories,
University of Minnesota,
September 10, 1926.

BOOK REVIEWS

Three Lectures on Atomic Physics. ARNOLD SOMMERFELD. Translated by HENRY L. BROSE.—This little book consists of three lectures delivered by Professor Sommerfeld at the University of London, and will be welcomed by theoretical physicits as being in a certain sense a supplement to his monumental "Atombau", for the lectures serve as an excellent summary of some of the most important recent developments in the quantum theory of line spectra. Naturally, in such a brief volume no attempt is made to discuss the mathematics of the new quantum dynamics, and instead more attention is given to some of their applications to spectroscopy. The first lecture includes the re-interpretation of the hydrogen and helium fine structure necessitated by recent theoretical developments and by refinements in experimental measurements of intensities. The second lecture is devoted to multiplet structures, including the quantum numbers proposed by Russell and Saunders, the definition of primed and unprimed spectral terms and their selection rules, and Pauli's principle of dissimilar quantum numbers. Simple, non-technical descriptions of this material have hitherto been rather scarce, and so Professor Sommerfeld's account is particularly welcome. The last lecture opens with the Smith-Stoner theory of the periodic table, and contains an interesting discussion of the nature of chemical linkage in tetrahedral crystal structures. The book is lucidly written, and not too technical. One cannot help but smile that the publisher should be so unfamiliar with Professor Sommerfeld's high standing in the world of atomic physics as to think it necessary to state in the blurb on the jacket that "Besides being an author himself, Professor Sommerfeld has annotated some of Einstein's writings on relativity!" E. P. Dutton and Co. 70 pp.

J. H. VAN VLECK

Crystalline Form and Chemical Constitution. A. E. H. TUTTON.—It is the purpose of this book to give a summary of Dr. Tutton's research on crystalline form which has extended over more than thirty years, and to show how the results of this research are related to the chemical constitution of the crystal and to the results of x-ray diffraction. The magnitude of the work which Dr. Tutton has done may be appreciated from the fact that he has made over 500 density determinations, has prepared more than 2,000 truly plane-faced section plates, and has measured over 45,000 crystal angles. His optical observations have been carried out for light from all parts of the spectrum for which the wave-lengths are accurately known. His work has meant the development of special instruments for grinding his crystals and for measuring their optical properties. These special instruments, together with his goniometers are described in some detail.

Dr. Tutton's work on isomorphism has completely confirmed Haüy's principle that no two crystals of dissimilar chemical compositions have exactly the same interfacial angles. He points out the importance of isomorphism in locating atomic weights and gives a very good résumé of the knowledge of overgrowth and mixed crystals. Many of the illustrations and examples in this portion of the book are from the author's wealth of experience in such matters. There is an equally good review of optical activity with references to the work of Sir William Bragg and his associates.

The writer is unable to agree with the author's ideas in connection with ionized crystal structure given on page 29. For instance, in discussing sodium chloride and similar crystals the author states that "the structure appears as if it were of atoms and not of molecules, although, of course, the molecules are really there, as they were deposited from the saturated solution as such." If this were so, molten NaCl could not be electrolyzed. Physical chemists agree that the sodium and chlorine are present in the

solution as *ions*, not as *molecules* of NaCl. Otherwise, solutions of NaCl would not be conducting. Apparently the work of Debye has removed the last objection to this viewpoint. If we once assume the existence of ions in solutions of NaCl, it is very reasonable to assume that the sodium and chlorine are deposited upon the space lattice of the growing crystal as ions.

It is unfortunate that the book has a rather unwieldy sentence structure. A typical example is the following: (page 50) "For the measurement of crystal angles the No. 2A Fuess horizontal-circle goniometer (reading to half-minutes) was, and remains unbeaten for convenience and accuracy; and the No. 1A Fuess larger instrument, reading to seconds is the most efficient instrument for refractive index measurement by the best of all methods, that of the 60°-prism when cut to afford two of the three indices of these rhombic and monoclinic salts directly, one afforded by light vibrating parallel to the refracting edge and therefore to one of the three axes of the optical-ellipsoid, and the other corresponding to vibrations perpendicular to the edge and parallel to a second of the principal axes of the ellipsoid."

In spite of this, however, the book is a very valuable book and should be on the shelf of everyone who is working with crystal structure. xii+252 pp., 72 figs., Macmillan & Co. New York City, 1926. Price 3.60.

WHEELER P. DAVEY

Polarisations-Mikroscop, seine Anwendung in der Kolloidforschung und in der Farberei. HERMANN AMBRONN UND ALBERT FREY.—This is Volume Five of the series of monographs on the investigation of colloids which is being edited by Richard Zsigmondy. This book deals with the technique of the polarization-microscope, especially in regard to its use in the study of colloids. The first half gives an introduction to the theory of polarization and double refraction without the use of difficult mathematics. It takes up the manipulation and adjustment of the polarization-microscope and the uses of the various compensators and other accessories. The directions and explanations are very clearly written and illustrated by a number of well-chosen figures. The second half of the book is divided into two sections, dealing respectively with the phenomena of double refraction in dispersoid systems, and the optical methods for determining their sub-microscopic fine structure. The variation of double refraction of the colloids with the indices of refraction of various imbibed liquids is a method of investigation discussed in detail. A number of practical examples are used as illustrations. The book ends with a discussion of the theory of coloring with dyes and with chemical elements in suspension. The book is well written and will be of great value to anyone desiring an introduction into this field of investigation. Pp. vii+195, 48 figs. Akademische Verlagsgesellschaft m.b.H. Leipzig, 1926. RM 13.50 bound; 12.—unbound.

JOSEPH VALASEK

Galilei und sein Kampf für die copernicanische Lehre. EMIL WOHLWILL.— In recent time two investigators have devoted themselves to the intensive study of the life and times of Galileo, based upon documentary material of which much had not been previously available to historians. One of these investigators was Antonio Favaro who edited the great twenty-volume national editon of the works of Galileo, and prepared life-histories of friends and correspondents of Galileo. The other was Emil Wohlwill who devoted some forty years to Galilean questions. His first volume appeared in 1909; he died in 1912, and left behind an incomplete second volume which has been prepared for publication by Friederick Wohlwill, with the cooperation of several other German scholars. Emil Wohlwill made a new and critical examination of all source material, with the view of eliminating what to him seemed mythical in Viviani's life of Galileo. Though many readers may not accept all of Wohlwill's conclusions, his work on Galileo is worthy of most serious attention. In some instances, Wohlwill and Favaro differ—for instance,

on the authenticity of the narrative of the public experiments on falling bodies from the leaning tower of Pisa. Wohlwill argues from Galileo's manuscript, entitled *De Motu*, which consists of lecture notes prepared while in Pisa, that in his early years Galileo was still under the influence of Aristotelian ideas to such an extent that he could not possibly have taken the public stand against Aristotle as described by Viviani. After examining the *De Motu*, the present reviewer is not able to agree with Wohlwill on this point.

The official documents relating to Galileo and the inquisition became known in 1867. In the second volume, the treatment accorded Galileo by the Inquisition is discussed in great detail and with marked fairness.

Erster Band, 1909, pp. xx+646. Zweiter Band, aus dem Nachlass herausgegeben, 1926, pp. xii+435. Verlag von Leopold Voss, Leipzig.

FLORIAN CAJORI

Die Welt der Atome. ARTHUR HAAS.—This book consists of ten lectures delivered at the University of Vienna during the summer semester of 1926, the general topics of which are these: electrons, ions, alpha-particles, disintegration of nuclei, radiation, analysis of spectra, the Bohr-Sommerfeld atom-model, the Periodic Table, interpretation of stationary states, molecules, radioactivity, and speculations about transmutation of matter and energy.

The lectures were composed for the "layman"—evidently the same wonderful German layman for whom Sommerfeld wrote the first edition of his "Atombau", and whose capacity for absorbing the data of physics undiluted might well be envied by many a professional physicist. There is not a trace of literary allusiveness or embellishment in the book; the only concession to the "layman" is the total avoidance of mathematics, carried even to the slightly absurd extent of writing the mass of the hydrogen atom as .00000000000000000000166 milligram and calling 10^{12} a billion (the American reader must remember the continental usage of the words *Milliard* and *Billion*). To illustrate the compact and literal quality of the presentation, here is a passage near the beginning (page 5): "As a unit of quantity of electricity we take in theoretical physics, for reasons not to be discussed further in this place, an electric charge which exercises upon a second equal charge one centimetre away a force equal to the pull upon a weight of 1.02 milligram; this unit charge is named the electrostatic unit."

With this condensed and undecorated style, the author succeeds in packing a remarkable amount of information into the book. His chief fault is the unquestioning presentation of the Bohr-Sommerfeld atom-model in its earliest form without the least intimation that it is tentative and may be transitory. In fact, two of his statements about the atom-model are already outmoded: the assignment of integer values to the azimuthal quantum-number for the permitted orbits in the model for the hydrogen atom, and the assertion that whenever an atom is in an S or P or D state its most loosely bound electron is in an orbit of azimuthal quantum-number 1 or 2 or 3. I have, however, found no mistakes of fact, except the statements that the spectra of the alkali metals contain singlet terms and that ninefold terms are known; possibly the latter of these is no longer a mistake. The intimation that the intensities of the various lines constituting a multiplet stand in integer ratios is much too strong. The reader should know that the assertion at the beginning of Chapter II ("the number of kinds of atoms is as great as the number of elements") is a false statement evidently made with full awareness and corrected seven pages further on ("the different kinds of atoms of an element are called isotopes"). There are other instances of this procedure; it would be dangerous therefore to stop reading in the middle of the book. Nevertheless, after all these objections are made, the richness and almost uniform reliability of the work still remain imposing. The illustrations are admirably chosen and reproduced. I can recommend the book, not indeed to the ordinary layman, but to the student of physics who is desirous of reviewing the knowledge which he has acquired or anticipating that which he expects

to acquire from treatises which have not been so thoroughly divested of the mathematical processes. Pp. xii+130, 37 figs. Walter de Gruyter & Co., Berlin and Leipzig. Price 4.80 R.M.

KARL K. DARROW

Physico-Chemical Methods. JOSEPH REILLY, WILLIAM NORMAN RAE and THOMAS SHERLOCK WHEELER.—The authors have produced this manual primarily as an aid to the industrial chemist or investigator, but partly also for the advanced student. An impressive feature of the book is its wide scope. One finds all of the ordinary subjects discussed, and in addition many less usual, including for instance, nomography, the design and equipment of the laboratory, photography, the microscope, the photo-electric effect, and x-ray analysis. The appeal to the techincal chemist is reflected in the appearance of such topics as the analytical distillation of butter fat. Exhaustive treatment of all the subjects discussed is manifestly impossible, yet those that, in the judgment of the authors, are most likely to be required, are fairly complete. In few cases is the treatment so perfunctory as to be of little value. On the other hand, trivial detail in text and figure is not always excluded. In appraisal of the book, there seem to be numerous minor criticisms of an adverse character possible, but few, if any, of major importance. Its good features seem greatly to outweigh the questionable ones. As to its usefulness to the workers it is designed to serve there can be no doubt. xi+735 pp., 453 figs., D. Van Nostrand Company, New York, 1926. Price 30s.

E. D. EASTMAN

Theory of vibrating systems and sound. IRVING B. CRANDALL.—This work is a text designed "to supplement rather than to replace the accepted treatises of sound". The supplementation is more than welcome. The author discusses many of the modern developments, such as problems of radiation, of transmission, and of architectural acoustics, but he gives fairly complete references to even a broader range of recent literature. The book has that freshness and forward outlook which might be expected from a research worker in the Bell Telephone Laboratories, where there are always consistently under way numerous and important investigations in acoustics. The student will find that the work is prepared in his interest. The text is clear and the problems add the opportunity of increasing one's comprehension.

The volume is limited to two hundred and sixty pages and consequently some of the recent fundamental contributions have necessarily been referred to with regrettable brevity. Most important among the omissions are the results of the investigations in the (author's own) Bell Telephone Laboratories. The title is intended to be specific and not to limit the meaning of "Sound," which correctly includes all mechanical vibrations. The value of the book for reference will be widely appreciated. x+260 pp., 24 diagrams, D. Van Nostrand Company, New York City, 1926. Price $5.00.

G. W. STEWART

Thermodynamics (For Students of Chemistry). C. N. HINSHELWOOD, M.A.—The following quotation from the preface will indicate the author's point of view. "I have done what I can to make the fundamental ideas of thermodynamics as clear as possible and particularly to explain the methods by which the abstract general laws are brought to bear upon the actual problems of physics and chemistry . . . . . A good deal of stress is laid, all through the book, on the interconnection between the law of thermodynamics and the kinetic theory . . . . . I am out of sympathy with those who regard thermodynamics as a science based upon empirical laws independent of the actual nature of things. If it were not for the molecular kinetic nature of things there is no particular reason for believing that the laws of thermodynamics would be what they are."

In this little volume the author discusses in an interesting manner the first and second laws, the Gibbs-Helmholtz equation, entropy and other thermodynamic func-

tions, conditions of equilibrium, the phase rule, the problem of chemical combination and finally the relation between entropy and probability. Whenever it is possible, the subject under discussion is "explained" in terms of the molecular-kinetic theory of matter.

For two reasons, however, the reviewer feels inclined to doubt the usefulness of this book to a student beginning the study of thermodynamics. In the first place, such students are likely to have only a confused notion of the distinct roles played by laws and by theories in the development of their science, and this book will hardly serve to dissipate the confusion. In the second place, a student who wants to master the subject, must train himself by the application of thermodynamic equations to concrete problems. Now a remarkable feature of the book under review is the almost complete absence of numerical data of any kind. It contains no heats of reaction, no specific heats, no equilibrium constants, no activity coefficients.

Finally we may remark that in the few pages devoted to Nernst's Heat Theorem, the unwarranted assumption is made that specific heats of solids can be expressed by a few terms of a power series with the temperature as the variable. 185 pp., 11 diagrams. E. P. Dutton & Co. New York, 1926. Price $1.80.

F. H. MacDougall

Surface Equilibria of Biological and Organic Colloids. P. Lecomte Du Noüy.—The scope of this volume published in the American Chemical Society Monograph Series will be made clear by the following list of chapter headings: technique, drop of surface tension of a colloidal solution as a function of time. monomolecular layer of serum constituents, sodium oleate, egg albumin, characteristics of immune serum, influence of colloids on the crystallization of sodium chloride, surface equilibrium of complex colloidal solutions, interfacial tension, surface viscosity, general conclusions. This monograph is devoted almost exclusively to a description of the experimental work carried out by the author in the laboratories of the Rockefeller Institute and to an exposition of his theories and hypotheses. Workers in this field will find the volume very readable and stimulating. Since the experimental work reported in this volume consisted in measurements of surface tension by the ring method, using an apparatus designed by the author, one would expect a critical discussion of this particular procedure. This is however entirely lacking, the author being content with the theory of the ring method in its most naïve form. 212 pp. 74 figs. 24 plates. Chemical Catalog Co., Inc. New York. 1926.

F. H. MacDougall

An Introduction to Surface Chemistry. E. K. Rideal.—In nine chapters, the author discusses the surface tension of liquids and of solutions, surface films of insoluble materials, liquid-liquid, gas-solid and liquid-solid interfaces, differences of potential at interfaces, conditions of stability in suspensions and emulsions, gels and hydrated colloids. While this volume contains a brief but excellent exposition of the facts and theories of what may be already called "classical" colloid chemistry, most readers will be interested chiefly in the chapters devoted to the properties and structures of surfaces.

In this connection, the author uses not only the resources of thermodynamics but also the theorems of kinetic theory and statistical mechanics in an admirable account of efforts to arrive at an intimate, molecular picture of surface layers and films. The reviewer is heartily in accord with the statement made by Dr. F. G. Donnan in his preface to this monograph that "every student and investigator of surface and colloid phenomena owes Dr. Rideal a warm debt of gratitude for his admirable survey and presentation of a great and rapidly advancing field of physico-chemical science." vi+336 pp. Cambridge University Press, 1926. Price 18s net.

F. H. MacDougall

Beyond the Milky Way. GEORGE ELLERY HALE.—This very interesting book is divided into three chapters dealing respectively with the ancestry of the telescope, the measurement of heat from the stars, and observations on spiral nebulae beyond the Milky Way. It summarizes in popular style the most important of the recent astronomical observations and theories. Recent radiometric measurements on stars are presented with a discussion of their significance. The last chapter deals with the theory of "island universes," and includes a brief discussion of cosmic rays and their possible origin. It is a fascinating book to read, and contains many fine illustrations.—Pp. xv+105, 44 figs. Charles Scribner's Sons, New York, 1926. Price $1.50.

JOSEPH VALASEK

Photometry. JOHN W. T. WALSH.—This is a very unusual book on this subject both in the choice of material and in its treatment. It does not contain details of planning lighting systems, or the uses of shades and reflectors, but deals rather with the measurement of illuminations, intensities of sources, and coefficients of transmission and reflection. Besides the usual photometric practice, the book contains a discussion of radiation theory, the eye and vision, spectro-photometry, physical photometry, and stellar photometry. At the end of each chapter is a very complete bibliography. This is valuable for anyone desiring to go more deeply into any of the subjects, for the author states that he has examined all journals on gas and electric engineering, illumination, physics, and general science, published in Great Britain, the United States, France, Germany, and Italy, from the first years of their publication. Under physical and stellar photometry are found discussions of the uses of photo-electric cells, thermopiles, bolometers, selenium cells, and photographic plates. Where these are incomplete, the excellent bibliography furnishes the key to further information. The material on standards of candle-power and standards of spectral distribution is also of great interest to those concerned with measurement of radiation. Although the book deals primarily with visible radiation, many of the physical spectro-photometric methods can obviously be extended to invisible radiation. There are a few mistakes; for example, the energy of photo-electrons is said to vary with the frequency of the light in a smaller ratio than "h." The errors are, however, of a minor character. The author has done a remarkable piece of work in bringing together this mass of information on photometric measurements. Many physicists, astronomers, and engineers will find much of value in this book. It is well written and contains many diagrams prepared with great care.—Pp. xxvii+505, 303 figures, D. Van Nostrand Company, New York, 1926. Price $10.00.

JOSEPH VALASEK